Tetrahedron Letters No.50, pp. 5091-5093, 1967. Pergamon Press Ltd. Printed in Great Britain.

A SELECTIVE CATALYST FOR THE HYDROLYSIS AND ESTER-EXCHANGE REACTIONS OF CARBOXYLIC ESTERS

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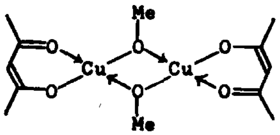
(Received in UK 27 August 1967)

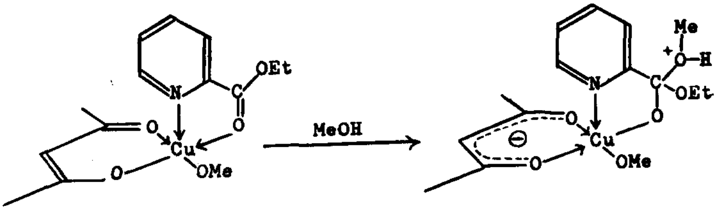
The preparation and physical properties of the dimeric chelate (I), bis(pentan-2,4-dionato)-µµ'-dimethoxydicopper(II), have been described by Bertrand and Kaplan.[1] We have found that this compound selectively catalyses the hydrolysis and ester-exchange reactions of carboxylic esters which have an amino nitrogen atom in the β- or γ-position and which are able to chelate with copper by using both the nitrogen atom and the ester group.



(I)

Ester-exchange reactions of ethyl picolinate in refluxing methanol, n-butanol, and iso-butanol, for example, proceeded to completion within 15 min. in the presence of catalytic concentrations (~1 mg./10 ml.) of the chelate; no reaction occurred in the absence of the chelate. Although the exchange reaction of ethyl 2-pyridylacetate in methanol was catalysed by the chelate to a less extent than the corresponding reaction with ethyl picolinate, the chelate was still a more effective catalyst than sodium methoxide in the former reaction. The chelate strongly catalysed exchange reactions of α-amino esters; with di-esters of glutamic acid only the exchange reactions of the α-ester group were catalysed, thus providing a convenient route to mixed esters of this acid. In contrast, the chelate had an almost neglible effect upon exchange reactions of esters of benzoic, nicotinic, isonicotinic, furoic, methoxyacetic, and thiomethoxyacetic acids. The ethyl esters of these acids were recovered unchanged after being refluxed for 15 min. with the chelate in methanol.

With all the exchange reactions which were catalysed by the chelate, rapid hydrolysis of the esters involved also occurred if water was present in the reaction mixtures. Methyl picolinate was completely hydrolysed when refluxed for 15 min. with an equivalent amount of the chelate in methanol which contained 2% (v/v) of water; no reaction occurred when the pyridine ester was replaced by methyl benzoate. In all the hydrolyses the product was the copper chelate of the expected carboxylic acid together with bis(pentan-2,4-dionato)copper(II). As these compounds were completely ineffective as catalysts, it was essential with ester-exchange reactions in which very small amounts of the chelate (I) were being used to employ carefully dried reagents and solvents, otherwise the water present rapidly destroyed the catalytic activity of the system.



(II)

It seems feasible that the dimeric chelate (I) functions as a catalyst in the reactions described above by dissociating to give the monomeric species which reversibly adds the carboxylic ester to form a chelate, e.g. (II), in which the ester group is co-ordinated with the copper atom. The co-ordinated ester group would be expected to react rapidly with water and alcohols, for the negative charge of the resultant dipolar species could be delocalised, as shown, by the pentan-2,4-dione anion. The remarkable selectivity of the catalyst obviously results from the requirements necessary for the ester group to become co-ordinated with the copper, and from the considerably higher affinity of copper(II) for ligands which bond through nitrogen than for those which bond through oxygen or sulphur. Other chelates which in the unsolvated monomeric state would contain tri-co-ordinated copper(II), e.g. N-acetatosalicylideneaminatocopper(II), show catalytic activity similar to the dimer (I); quantitative comparisons will be made elsewhere.

The results outlined in this Letter cast doubt upon the validity of the ionic mechanisms which were proposed[2,3] for the hydrolysis and ester-exchange reactions of the chelates obtained by condensation of bis(salicylaldehydato)copper(II) with α-amino esters and with esters of β-amino alcohols. It now seems likely that these reactions proceed *via* non-ionic species analogous to (II).

References

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2. R. P. Houghton and D. J. Pointer, *J. Chem. Soc.*, 3302 (1964).
3. R. P. Houghton and D. J. Pointer, *J. Chem. Soc.*, 4214 (1965).