

## Kinetics and mechanism of metal ion catalysed hydrolysis of methyl glycinate

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Hydrolysis of methyl glycinate in the presence of  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Zn}^{2+}$  is second order in  $[\text{OH}^-]$  and zero order in [ester]. The reaction rate increases with increase in  $[\text{M}^{2+}]$ . A mechanism involving the formation of a tetracoordinated metal chelate between the metal ion and the ester has been proposed. Amongst the four metal ions studied  $\text{Cu}^{2+}$  seems to be the most efficient.

It has been observed<sup>1-10</sup> that metal ions such as  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Zn}^{2+}$  efficiently catalyse the hydrolysis of amino acid esters. Presently an attempt has been made to study the title reaction systematically from kinetic point of view.

### Experimental

Glycine methyl ester hydrochloride was prepared according to the method described elsewhere<sup>11</sup> and its purity checked by its melting point and spectral data.  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (AR, E. Merck) were used as such.

The rates of alkaline hydrolysis of glycine methyl ester in the absence and presence of various metal ions were measured by determining the rate of disappearance of  $[\text{OH}^-]$ . The procedure consisted of mixing definite volumes of thermally equilibrated solutions of ester and metal ion to which NaOH solution was already added so that the final reactant solution was about 50 ml with pH in the range of 7.5-8.5. In order to measure the amount of hydroxide ion present in the experimental solution at any instant the pH values of the solutions were measured for about  $1 \frac{1}{2}$  hr with a pH meter (Electronic Instruments Ltd, model 7020).

### Results and discussion

Under the condition  $[\text{ester}] \gg [\text{OH}^-]$  and pH in the range 7.2-7.8 the reaction follows a second order kinetics in  $[\text{OH}^-]$ . The reaction rate was found to be insignificant in the absence of metal ions. Order in [ester] was zero.

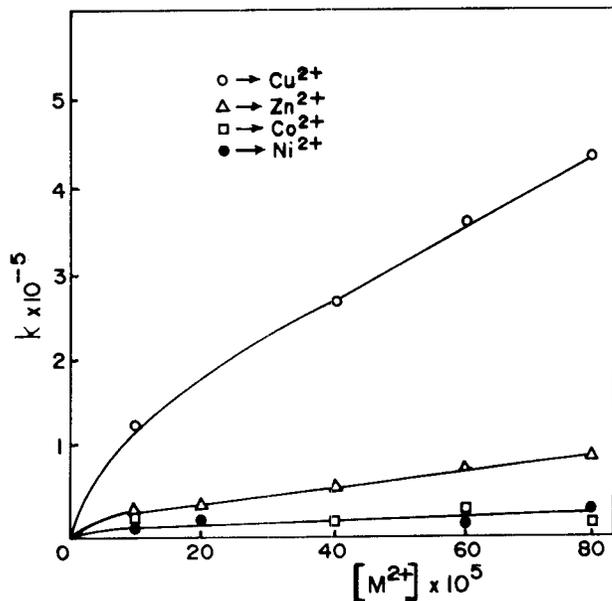
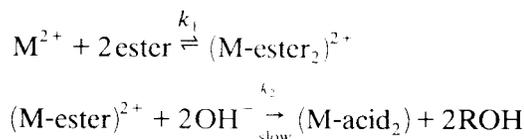


Fig. 1—Plot of rate constant versus  $[\text{M}^{2+}]$ .

Figure 1 shows the variation of rate constant with  $[\text{M}^{2+}]$ . The reaction rate increases with increase in the metal ion concentration.

It may be mentioned that our results are not in agreement with those of Kroll<sup>1</sup> and others<sup>2</sup>. They claimed to have found a first order dependence on [ester] and first order in  $[\text{OH}^-]$ . However, we have proved beyond doubt the reaction obeys second order kinetics in  $[\text{OH}^-]$ .

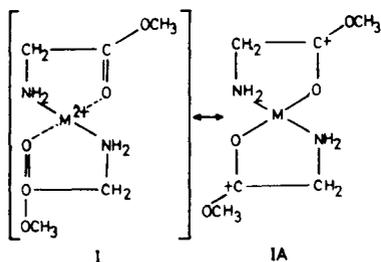
The facts that hydrolysis reactions of ordinary esters are not catalysed by metal ions but those of amino acid esters are, seem to indicate that for metal ion-catalysed hydrolysis, in addition to carbonyl group, a second coordination site is essential to be present in the ester molecule. Thus the common feature in the mechanism involving all the metal ions studied is that an amino acid ester chelates with a metal ion and the metal ion chelate thus formed is attacked by  $\text{OH}^-$  in a slow step (Scheme 1).



Scheme 1

The initial step of chelate formation is similar to that proposed by Kroll<sup>1</sup> except that two molecules of ester have been assumed to react instead of one

to give the chelate. Metal ester complex is supposed to have the resonance structures I and IA. The C-O-M angle in I is in theory close to  $120^\circ$ , an angle leading to considerable strain in the ring. On the otherhand, the angle C-O-M in IA is about



$109^\circ$ , a value much closer to the theoretical angle ( $108^\circ$ ), for a symmetric five-membered ring. Ring strain is thus reduced and therefore structure IA is presumed to be the important resonance structure. In the slow step two  $\text{OH}^-$  ions are involved to complete the reaction. Instead of free acids metal-acid complex has been proposed as the final product because metal complexes of amino acids are quite stable especially in alkaline medium. It is known that carbonyl oxygen of the carboxylate anion is a better coordinating agent than both free acids and esters. The mechanism in Scheme 1 leads to rate law (1).

$$dx/dt = k_2[(\text{M-ester}_2)^{2+}][\text{OH}^-]^2 \quad \dots (1)$$

Applying steady state approximation and also writing the total metal ion concentration as

$$[\text{M}^{2+}]_0 = [\text{M}^{2+}] + [(\text{M-ester}_2)^{2+}] + [\text{M-acid}_2]$$

where  $[\text{M}^{2+}]_0$  stands for initial metal ion concentration and  $[\text{M}^{2+}]$  for free metal ion concentration, we get rate expression (2).

$$dx/dt = \frac{k_2\{k_1[\text{M}^{2+}]_0 - k_1[\text{M-acid}_2]\}[\text{ester}]^2[\text{OH}^-]^2}{k_1[\text{ester}]^2 + k_{-1} + k_2[\text{OH}^-]^2} \quad \dots (2)$$

Under the present experimental conditions,  $[\text{ester}]$  is much larger than  $[\text{OH}^-]$ . ( $[\text{ester}] \approx 10^3 [\text{OH}^-]$ ). Hence  $k_{-1} + k_2[\text{OH}^-]^2$  can be neglected. Thus we obtain

$$dx/dt = k_2\{[\text{M}^{2+}]_0 - [\text{M-acid}_2]\}[\text{OH}^-]^2 \quad \dots (3)$$

If the metal ion concentration is large and the reaction has not progressed too far, the above mechanism predicts a second order dependence in  $[\text{OH}^-]$  and zero order in  $[\text{ester}]$  as has been found experimentally.

The effect of  $[\text{metal ion}]$  on the reaction rate is shown in Fig. 1. The rate constant increases with increase in  $[\text{M}^{2+}]$ ; however the increase is not linear as is expected from the proposed mechanism because of the progressive increase in  $[\text{M-acid}_2]$ .

Amongst the four metal ions studied viz.  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$  seems to be the most efficient, in general agreement with the results obtained by Hix and Jones<sup>12</sup> and also by other workers who have correlated the catalytic efficiency with the stability of metal-ester complexes.

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