# The Effect of π-Bonding Ligands on the Metal Ion-catalysed Decarboxylation of Acetonedicarboxylic Acid

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THE uncatalyzed and transition-metal ion-catalyzed decarboxylation of acetonedicarboxylic acid,

$$HO_2C{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CO_2H \rightarrow CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO_2H + CO_2$$

has been studied in some detail by Prue.[1] Rund and Plane[2] have recently found that unsaturated ligands such as *o*-phenanthroline which are capable of $\pi$-bonding with metal ions, enhance the catalytic activity of manganese(II) by a factor of 16 in the metal ion-catalysed decarboxylation of αα-dimethyloxaloacetic acid. The effect with nickel(II) was quite small (2 ×). Dicarboxylic β-oxo-acids are ideal substrates for studies of this type of catalysis as they form charge neutral 1 : 1 complexes of the MA type with the dianions of the acids ($A^{2-}$) and bivalent metal ions ($M^{2+}$) and there is little tendency to form bis-complexes.[3,4]

The metallo-decarboxylases are generally manganese(II)- or magnesium(II)-dependant enzymes. In the metal ion-catalyzed reactions, manganese(II) is a rather poor catalyst. Thus in the decarboxylation of oxaloacetic acid the values for $10^2k_{MA}$ at 25° (sec.$^{-1}$ units) are 6·6 [copper(II)]; 2·3 [nickel(II)]; 2·4 [cobalt(II)]; and 0·65 [manganese(II)]. The copper(II) complex decomposes ten times faster than the corresponding manganese(II) complex. In view of Rund and Plane's findings we have studied the effect of 2,2′-bipyridyl on the decarboxylation of acetonedicarboxylic acid and have obtained similar results. Complexes such as (I) are roughly twelve times more active than the corresponding aquo-complexes (II) in decarboxylation.

In the case of the copper(II) and nickel(II) complexes the effects are relatively small (2 ×). The values of the rate constants obtained are summarized in the Table. The decarboxylation is first order in the carboxylic acid, and the *pseudo*-first-order rate constant ($k_{obs}$) is given by the expression $k_{obs} = k_u + k_{cat}[M^{2+}]$ where $k_u$ is the rate constant for the spontaneous decarboxylation and $k_{cat}$ the catalytic rate constant.

TABLE

*Catalyzed decarboxylation at* 42°

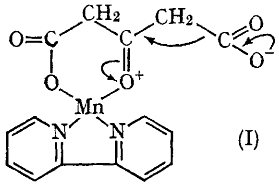
(Ionic strength = 0·1M, all rate constants obtained manometrically.)

| Catalyst | $k_{cat}$(mole$^{-1}$ min.$^{-1}$) |
|---|---|
| Cu$^{II}$ | 24[a] (22·8) |
| Cu$^{II}$ + 2,2′-bipy[b] | 48 |
| Ni$^{II}$ | 0·33 |
| Ni$^{II}$ + 2,2′-bipy[b] | 0·53 |
| Mn$^{II}$ | 0·012 |
| Mn$^{II}$ + 2,2′-bipy[b] | 0·12 |

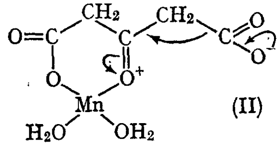
[a] Average value obtained for seven runs in the pH range 4·66—3·55 using 0·1M-acetate buffer. The value in parenthesis was obtained by Prue (ref. 1) at 42° and 0·1M-acetate. The value of $k_{cat}$ at 0·3M-acetate is 13·2 mole$^{-1}$ min.$^{-1}$, acido-complexes, are as expected, less active than aquo-complexes (*cf.* ref. 1).

[b] Equimolar M$^{II}$ and 2,2′-bipyridyl.

As suggested by Rund and Plane the greatly enhanced activity with manganese(II) may be due to some back $\pi$-bonding from the metal to the 2,2′-bipyridyl ring system, thus allowing the metal ion to have a higher effective charge when co-ordinated to 2,2′-bipyridyl than when co-ordinated to water. The smaller nuclear charge of manganese(II) conceivably allows greater back donation than with nickel(II) or copper(II). Obviously such effects may be important in the metallo-enzymes if the metal ion acts as a bridge between the substrate and the protein, and there is interaction between the metal ion and an appropriately located imidazole ring of a histidine residue.



(I)



(II)

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