Formation Constants of the Complexes of Some Prop-2-enoates

and Pent-4-enoates with Cu(II)

By

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Abstract.- This paper deals with the determination
of dissociation and stability constants of the
Cu(II) complexes of some prop-2- and pent-4-enoates
by pH-metric method.

The interaction of Cu^{2+} with substituted benzoic acids
has been studied in 50% dioxane-water mixture.[1] Pethe and
Mali[2] extended the study for some lanthanides with methoxy
substituted benzoic acids. Complexing ability of thio-
carboxylic acid has also been studied potentiometrically.[3]

The present work is a continuation of our earlier
studies on the complexation of some itaconates and cinnamates
with Cu(II) and is undertaken in an attempt to find out
whether the aromatic residue has an effect on the complexes
formed.[4]

Experimental.- The ligands (E) (naphthyl/COOMe) methyl
2-o-carboxyphenyl-3-(1- and 2-naphthyl)prop-2-enoates I and
II, respectively, and (E) 4-methoxycarbonyl-3,3-dimethyl-
5(1- and 2-naphthyl)pent-4-enoic acids III and IV, respectively,
have been prepared according to the methods adopted in the

literature.[5] Their purity were ascertained from their meltin
points. The structures of these compounds were established
and inferred.[5]

Measurements technique.- A PYE Unicam pH meter Model
290, in conjugation with glass calomel electrode assembly
was used for pH measurements. Potassium hydrogen phthalate
buffers were used to standardise the pH meter. All the re-
agents used were Analar, BDH and the titrations were carried
out in a thermostated closed cell at $25 \pm 0.1^{o}C$ in a nitrogen
atmosphere. Dioxane was purified before use by the standard
method.[6] Carbonate-free sodium hydroxide solution was pre-
pared and standardised potentiometrically against standard
potassium hydrogen phthalate. The complex solutions were
prepared by adding 50 ml of 0.01M solution of the ligand in
dioxane to 50 ml redistilled water containing 0.003M copper
perchlorate and 0.02931M perchloric acid. 0.5M sodium
hydroxide was used for the titration.

The nature of dissociation of the ligands was measured
potentiometrically in 50% v/v aqueous dioxane at 25°. From
the titration curves the dissociation constants of the
ligands pK_L were determined. The values obtained are given
in Table 1. The metal-ligand stepwise stability constants
have been determined by Bjerrum-Calvin titration technique.[7,]

Results and Discussion.

The successive constants are calculated following
Poulsen et al.[9] method. From the titration curves, $\bar{n}$,

the average number of ligands bound to the central-metal
ion and A, the concentration of the free ligand species
in solution could be calculated.

From the titration curves it is observed that the
metal-ligand curves are well separated from the ligand
titration curves proving that the liberation of protons
is due to chelation. The formation curves (Fig. 1) for
the complexes formed by Cu(II) with ligands I - IV show two
inflection at $n \simeq 1$ and $n \simeq 2$ indicating the stepwise forma-
tion of 1:1 and 2:1 molar ratio of L:M. The stepwise forma-
tion constants K_1 and K_2 have been determined graphically
following the method adopted by Poulsen et al.[9] The values
of pK_{LM} were calculated graphically according to the method
given by Calvin and Wilson[7] and also by Uitert and Hass[10].
The values of $\log K_1$, $\log K_2$ and pK_{LM} for the complexes at
25° are tabulated in Table 1.

Table 1

Stability Constants of Cu(II)-Ligand Complexes and Dissociation
Constants of Ligand at 25°

Ligand	pK_L	pK_{LM}	$\log K_1$	$\log K_2$	$K_{(av)}$
I	6.10	6.00	3.29	3.04	1461
II	6.37	5.88	3.24	2.99	1302
III	7.04	6.59	3.08	2.83	878
IV	6.88	6.47	3.12	2.90 ·	1076

From the results obtained, it is observed that the
stability constants of copper complexes of the ligands under

investigation decrease in the order :

$$I > II > IV > III$$

The increase of the stability of the copper complexes of compounds I and II than those of compounds III and IV is attributed to the presence of the electron-withdrawal phenyl group which inhances the capacity of complexation.

Moreover, the coplanarity of the phenyl group makes the metal-ligand ring comparatively more stable than the methyl group. The electron-withdrawing phenyl group pulls electrons from Cu(II) ion, increases its back donation and hence the stability of the complex. This group withdraws electrons away from the proton in the parent acid resulting in a larger dissociation constant. The presence of the electron-donating alkyl groups increases the bond stability between the acid anion and the proton, thus decreases the back donation between the anion and the Cu(II) ion producing a less stable complex and smaller stepwise formation constants. The larger dissociation constant of 1-naphthyl derivative (I) than 2-naphthyl-(II) is in harmony with the naphthoic acids where the dissociation constants of 1- and 2-naphthoic acids are 2.00×10^{-4} and 6.80×10^{-5}, respectively. However, the presence of alkyl group probably makes the dissociation of 2-naphthyl derivative and the complex formed by this ligand larger than the 1-naphthyl derivative. The negative free energies of activation indicates that such complexation takes place spontaneously (Table 2).

Table 2

Free Energies for Stepwise Formation of Cu(II) Ligands at 25°

Ligand	log K_1	$-\Delta G^\circ$	Log K_2	$-\Delta G^\circ$
I	3.29	4.516	3.04	4.1717
II	3.24	4.444	2.99	4.1061
III	3.08	4.2207	2.83	3.8848
IV	3.12	4.2784	2.90	3.9767

The metal-ligands formula is suggested as follows

I - II

III - IV
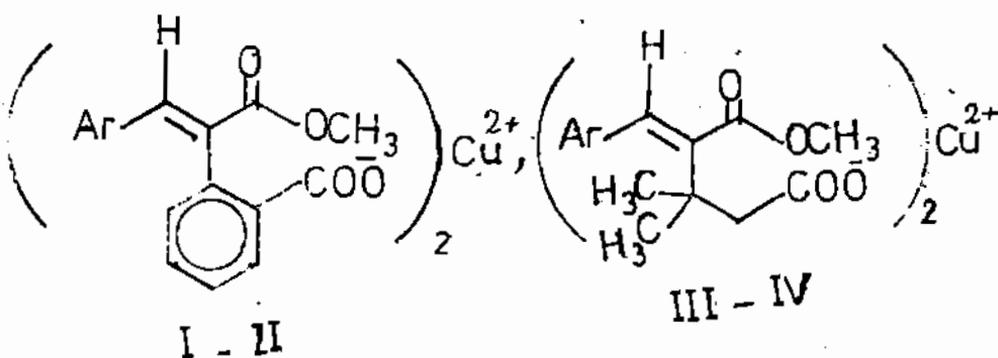
Ar = 1- or 2-Naphthyl

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