# Acid Dissociation Constants of Some Acetoacetarylthioamides & Stability Constants of Their Copper(II) & Nickel(II) Chelates

BARSOUM N BARSOUM* & MAGDI M NAOUM

Department of Chemistry, Faculty of Science,
University of Cairo, Giza, Egypt

Acid dissociation constants of acetoacetarylthioamides (Ia-d) have been determined potentiometrically in 50% (v/v) aq. dioxan. Stability constants of their Cu(II) and Ni(II) chelates have been related to the Hammett's substituent constants as well as the acid dissociation constants of the ligands.

In an earlier publication[1] from our laboratory acid dissociation constants of some acetoacetarylthio-amides and stability constants of their iron(III) and cobalt(III) chelates were determined spectrophoto-metrically in aqueous ethanol. The present note describes the potentiometric determination of the acid dissociation constants (pK_a) of acetoacetylthioamides (Ia-d) and the metal-ligand stability constants (log k_1 and log k_2) of their copper(II) and nickel(II) chelates in 50% (v/v) dioxan-water medium.

$$CH_3COCH_2CSNHC_6H_4X$$
$$(I)$$
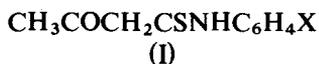
(a) p-CH$_3$O; (b) p-CH$_3$; (c) H; and (d) p-Cl

The ligands (Ia-d) were prepared by the method described earlier[1], recrystallized from benzene/pet. ether (40-60°) and dried *in vacuo*. Metal nitrates (BDH) were used for preparing metal ions solutions and the solutions were standardized titrimetrically using

EDTA. Dioxan was purified as described by Weissberger and Proskauer[2].

pH-measurements were made at 25°C on an Orion pH-meter equipped with saturated calomel electrode and sealed glass electrode. The pH-meter readings were converted into [H$^+$] using Van Uitert relation[3].

For determination of proton-ligand stability constants, the ligand solutions (0.1 M; 50 ml) were titrated against carbonate-free NaOH (0.1 M) at μ = 0.1 M (NaCl), while for determining the stability constants of Cu(II) and Ni(II) chelates, solutions containing NaCl (0.1 M), metal salts (10^{-3} M) and chelating agents (5×10^{-3} M) were titrated against 0.1 M sodium hydroxide. The degree of complex formation ($\bar{n}$), and the concentration of the free ligand anion [L$^-$] were calculated as described previously[4]. The stability constants of the complexes were obtained from formation curves. The pL^- values at $\bar{n}$ = 0.5 and 1.5 corresponded to log K_1 and log K_2, respectively[5]. These values were further refined by the method of least squares[6]. After K_1 and K_2 were obtained as above, [L$^-$] was calculated for $\bar{n}$ in the range of 0.1 to 1.9 using the equation[7]:

$$(2-\bar{n})K_1 K_2 [L^-]^2 + (1-\bar{n})K_1 [L^-] - \bar{n} = 0$$

and compared with the experimental values. The good agreement between calculated and experimental values indicates that polynuclear species and hydroxy or chloro complexes are not significant in these systems. The probable formation of the metal hydroxide, as well as the lower solubility of the tris-ligated complexes, caused precipitation of the solids at earlier stages during some of the titrations before complete range of $\bar{n}$ was studied (pH > 7). Thus it was not

Table 1—Acid Dissociation Constants of Ligands and
Stability Constants of Their Metal Chelates

[Medium: 50% aq. dioxan; μ = 0.1 M (NaCl)]

Substituent X	a	pK_a	Cu(II)		Ni(II)	
			log K_1	log K_2	log K_1	log K_2
p-CH$_3$O	−0.27	8.83	7.25	5.35	7.18	5.38
		(11.73)*	(8.17)	(6.85)		
p-CH$_3$	−0.17	8.73	6.90	5.10	6.66	4.78
		(11.62)	(8.28)	(6.85)		
H	0.00	8.58	6.25	4.09	6.17	4.33
		(11.45)	(8.00)	(6.68)		
P-Cl	+0.23	8.43	5.96	3.78	5.75	2.95
		(11.17)	(7.81)	(6.71)		

*Values for the corresponding oxygen analogues[12] are given in parentheses.

possible to obtain values for $\log K_2$ directly from results of $\bar{n} = 1.5$, but they were indirectly calculated from $\log K_{av}$ at values of $\bar{n} = 1$.

The data in Table 1 reveal that the acidity of the ligand depends on the nature of the substituent. The plots of pK_a against the Hammett's substituent constants[8] (σ) were linear.

The stability constants, $\log K_1$ and $\log K_2$, of copper(II) and nickel(II) chelates are presented in Table 1. The $\log K_1$ and $\log K_2$ values for the copper(II) chelates of the corresponding oxygen analogues are also included in Table 1 for comparison.

The applicability of the Hammett's equation to $\log K_n$ values was evident from the linear plots of $\log K_n$ versus the Hammett's substituent constants (σ).

The plots of stability constants against pK_a values were also linear indicating that the complex forming tendency of an anion is a function of its base strength. This behaviour is expected for a structurally similar series of compounds where steric effects of a particular substituent group are absent[9]. The values of $\log K_1/K_2$ (1.5-2 log units) for this series are well within the normal range, indicating that there is no steric interference to the addition of the second ligand group[10].

A comparison of acid dissociation constants of the ligands with those of their oxygen analogues (Table 1) indicates that the sulphur compounds behave as stronger acids than the corresponding oxygen analogues[11]. Consequently, the stabilities of the metal chelates with β-ketothioanilides are expected to be less stable than those of the corresponding chelates with β-ketoanilides[12]. This is found to be true (see Table 1).

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