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Copper(II) Chelates with Some Photographic Color Intermediates. Structure-Stability Relationships

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Acid dissociation constants, pK_1, of a series of benzoylacetanilides (Ia—i) have been determined potentiometrically in 50 vol% ethanol-water media at 30 °C. The stability constants, log β_1, of their copper(II) chelates have also been determined. The effects of substituents on the anilide moiety of the ligand on the equilibria are discussed. The data were correlated by the equations: $\mathrm{p}K_1 = 9.39 - 0.916\,\sigma$; $\log\beta_1 = 1.34\,\mathrm{p}K_1 - 5.42$; and $\log\beta_1 = 7.20 - 1.44\,\sigma$. These results were taken to imply that the stabilization by dative metal-to-ligand π-bonding is not significant in copper(II)-benzoylacetanilide complexes.

Benzoylacetanilides (I) are useful intermediates in the color photographic process.[1] The chelating ability of these compounds to form stable metal chelates has recently elicited interest. Syntheses of iron(III),[2] copper(II),[3] oxo-vanadium(IV),[4] dioxo-molybdenum(III),[5] dioxo-uranium(VI),[6] titanium(IV),[7] and chromium(III)[8] complexes, and reports concerning the estimation of titanium, vanadium, and mercury[4,7,9] are all that have appeared so far. In continuation of our studies on the relationship between structure and properties of I,[10,11] we have investigated the effects of substituents on the chelating tendency of a series of benzoylacetarylamides (Ia—i) towards copper(II). The acid dissociation constants and stability constants of these ligands and copper(II) cation were determined potentiometrically in 50 vol% ethanol–water solution at 30 °C ±0.1.

$$C_6H_5COCH_2CONHC_6H_4R$$

I

a, R=4-MeO
b, R=4-Me
c, R=3-Me
d, R=H
e, R=3-MeO
f, R=4-Cl
g, R=3-Cl
h, R=3-Br
i, R=4-EtOOC-

The object of the present work was, on one hand, to test the applicability of the Hammett equation to correlate the stability constants of copper(II)–benzoylacetanilide complexes, and on the other, to determine the extent of copper(II)-ligand π-bonding in such chelates.

Experimental

Benzoylacetanilides (Ia—i) were prepared by condensation of equimolecular amounts of ethyl benzoylacetate and the appropriate aniline as previously described.[12] The physical constants of the compounds prepared agreed with those in literature.[12,13] The stock solution of each anilide was prepared by dissolving the appropriate weight of the anilide in ethanol.

Absolute ethanol (BDH AnalaR reagent) was used. Carbonate-free sodium hydroxide solution was prepared in 50 vol% ethanol-water. A stock solution (0.1 M) copper nitrate was prepared in doubly distilled water and the copper (II) concentration was determined by standardization with EDTA using Eriochrome Black-T as indicator.[14] A solution of potassium nitrate (0.5 M) was also prepared in 50 vol% ethanol–water.

Titrations were performed using a Radiometer pH meter (type 63) equipped with a combined glass electrode type GK 2311C. The thermostated vessel of 50 ml capacity was tightly covered with a special electrode head through which passed the glass electrode, the nitrogen inlet tube and the delivery tube from the auto-burette. Auto-burette type Metrohm Herisau Multi-Dosimat E 415, accurate to ±0.01 ml was used.

In a typical titration, a 25 ml solution was prepared by mixing the appropriate volume of the ligand solution, 5 ml of potassium nitrate solution, and 0.25 ml of copper(II) solution, and the mixture was diluted to the mark. The concentration of copper(II) was always 1×10^{-3} M and those of ligand were 1×10^{-3} and 2×10^{-3} M. The solution was then transferred to the titration cell. A stream of nitrogen gas, traces of oxygen and carbon dioxide being removed by the method of Albert and Serjeant[15], was bubbled through. A complete titration consisted of successive addition of 0.05 ml or less of the titrant. One minute to two minutes after each addition, the pH meter reading was recorded. The titration was continued up to pH∼7.00 in most cases. Visual precipitation occurred at pH∼6.50. Each titration was repeated at least twice giving reproducibility of ±0.01 pH units along the titration. The pH readings were caliberated before, and checked after each titration using standard Radiometer buffers of pH's 4.01±0.01 and 7.00±0.01.

Calculated amounts of nitric acid and sodium hydroxide were used to check the pH in 50 vol% ethanol–water. A calibration curve was made and corrections for pH's were recorded.

Results and Discussion

The potentiometric titration curves for some of the ligands studied are illustrated in Fig. 1. No clear inflection was observed at all in the neutralization of these active methylene ligands. The acid dissociation constants of these reagents were calculated from the titration curves as follows. The pH meter readings (B) in 50 vol% ethanol–water solution are converted to hydrogen ion concentration [H$^+$] by means of the widely used relation,[16] namely:

$$-\log[\mathrm{H}^+] = B + \log U$$

where U is the correction factor. The value of $\log U$ in 50 vol% ethanol–water medium at 30 °C was determined and was found to be −0.35. The pK_1 value of the ligand HL was then calculated using the equation:

$$K_1 = \frac{(aT_\mathrm{L} + [\mathrm{H}^+] - [\mathrm{OH}^-])[\mathrm{H}^+]}{T_\mathrm{L}(1-a) - [\mathrm{H}^+] + [\mathrm{OH}^-]}$$

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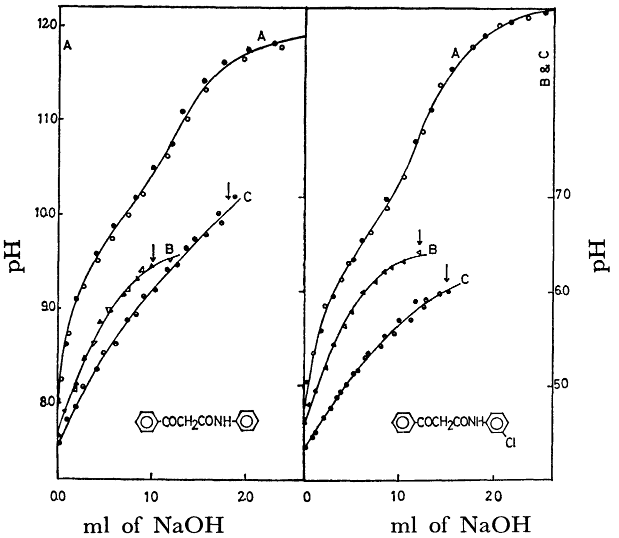


Fig. 1. Titration curves of some benzoylacetanilide-copper(II) systems in 50 vol% ethanol-water media at 30 °C, μ 0.1.
●○: ligand alone, $1.0\times10^{-}$ M
△▲: $[HL]=[Cu^{2+}]=1.0\times10^{-3}$ M
◒◓: $[HL]=2.0\times10^{-3}$; $[Cu^{2+}]=1.0\times10^{-3}$ M.

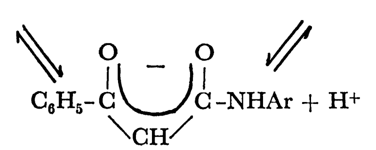
Table 1.

Ligand	σ	$pK_1 \pm s^{a)}$	$\log\beta_1 \pm s$	$S_f^{b)}$
Ia	−0.27	9.68±0.03	7.56±0.03	+0.57
Ib	−0.17	9.60±0.05	7.41±0.05	+0.34
Ic	−0.07	9.45±0.04	7.22±0.05	0.00
Id	0.00	9.43±0.02	7.24±0.02	0.00
Ie	+0.05	9.40±0.03	7.10±0.06	−0.17
If	+0.23	9.20±0.03	6.89±0.04	−0.58
Ig	+0.37	9.11±0.02	6.73±0.06	−0.83
Ih	+0.39	9.10±0.02	6.80±0.05	−0.77
Ii	+0.45	8.98±0.04	6.64±0.05	−1.05

a) s=standard deviation. b) S_f=stabilization factor

where a is the ratio of the mole base added to mole of ligand. The results of the computations are given in Table 1.

The pK_1 values, so obtained, correspond to the overall dissociation constant of the two tautomers of benzoylacetanilide as given by the equation:



$$C_6H_5\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-NHAr \rightleftharpoons C_6H_5-\overset{O-H}{\overset{|}{C}}=CH-\overset{O}{\overset{\|}{C}}-NHAr$$

$$\rightleftharpoons C_6H_5-\overset{O}{\overset{|}{C}}\underset{CH}{\overset{-}{\frown}}\overset{O}{\overset{|}{C}}-NHAr + H^+$$

The data show that the magnitude of the pK_1 value of I depends on the nature of the substituent on the anilide ring. Electron withdrawing groups increase the acidity whereas electron-donating ones have an opposite effect. The relationship between the acidity constants, pK_1, and the Hammett substituent constant, σ, is shown in Fig. 2. It is obvious that the pK_1 values of the series studied are fairly correlated with σ constant. Using the least squares method, the values of the slope, ρ, and the intercept, pK_1, were found to be 0.916 and 9.39 respectively (correlation coefficient, r=0.989). The value of the reaction constant, ρ, so obtained, is somewhat higher than that (ρ=0.741) reported by Pelizzetti *et al.*[17] for related series of anilides. This difference is undoubtedly due to solvent effects.[18] The latter authors have evaluated the value of the reaction constant from measuring the dissociation constants spectrophotometrically at 25 °C in aqueous solutions containing less than 1% organic solvent.

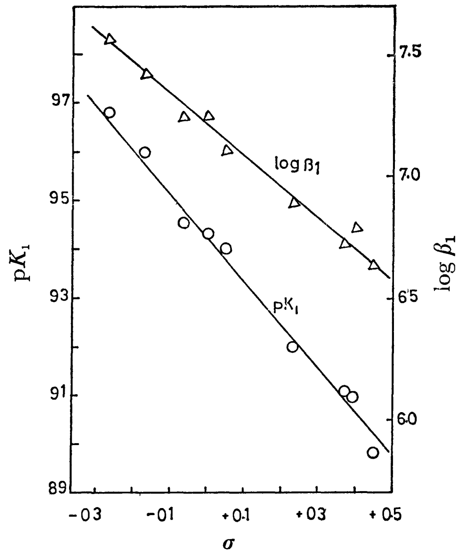


Fig. 2. Correlation of pK_1 and $\log\beta_1$ with Hammett substituent constant, σ.

The potentiometric titration curves for copper(II)-benzoylacetanilide systems (1 : 1; 1 : 2) are illustrated in Fig. 1. Similar curves were obtained for other systems investigated. The low solubility of the 1 : 2 Cu(II) chelates caused early precipitation during many of the titrations. Thus the stability constant, β_1, for the 1 : 1 complex species only was calculated and compared. This constant was calculated using the equation:

$$\beta_1 = \bar{n}/(1-\bar{n})L$$

where

$$L = ((1-a)T_L-[H^+])/([H^+]/K_1)$$

and

$$\bar{n} = T_L-(L([H^+]/K_1)+1))/T_M.$$

In these equations T_L and T_M correspond to the total ligand and metal ion concentrations used respectively, and $\bar{n}$ is the average number of ligand bound to the metal ion. The calculated values of log β_1 are summarized in Table 1.

As the relation between Cu(II) and these ligands is regarded as a Lewis acid-base reaction, the log β_1 value is plotted against the acid dissociation constant, pK_1, in Fig. 3. As shown, the log β_1 values are linearly related to the pK_1 values. This implies that the stability of the chelates is mainly dependent upon the basicity, *i.e.*, the pK_1 value, of the ligand. A slope value of 1.34 of the straight line obtained (Fig. 3) was found as calculated by the least squares method. This result suggests that Cu(II) in the complexes studied does

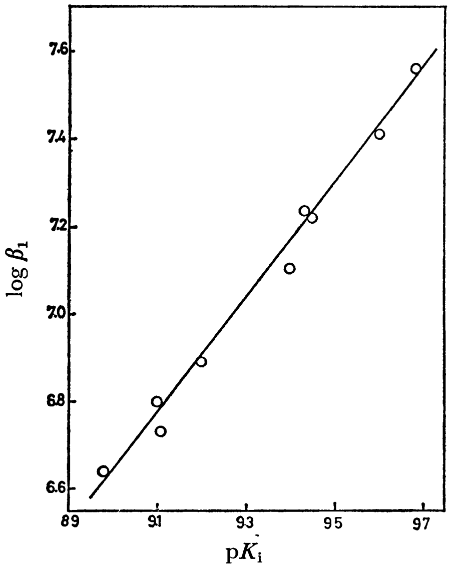


Fig. 3. Relation between acid dissociation constants of benzoylacetanilides, pK_1, and stability constants, $\log \beta_1$, of their copper(II) chelates.

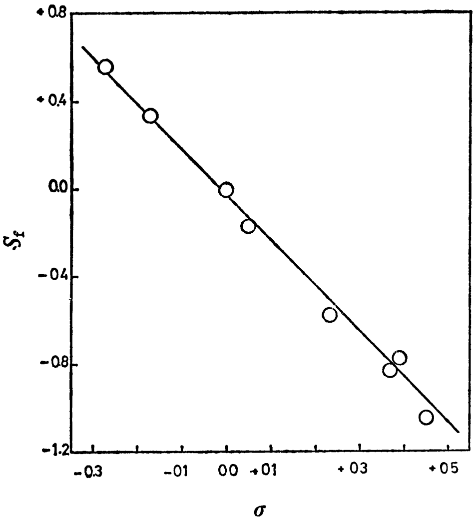


Fig. 4. Correlation of stabilization factor, S_f, with Hammett substituent constant, σ, for 1 : 1 complexes of copper(II) with benzoylacetanilides.

not function as π-electron donor, as it was suggested for copper(II) complexes with substituted benzoic acids.[19] If the 1 : 1 complexes of benzoylacetanilides with Cu(II) were stabilized by back-electron donation from the metal ion to the ligand, the slope of the plot of $\log \beta_1$ *vs.* pK_1 should be less than unity.[20]

In order to confirm the foregoing conclusion, the stability constants, $\log \beta_1$ (Table 1), were correlated with the Hammett substituent constant, σ. Figure 2 shows such a correlation. The equation of the straight line obtained is:

$$\log \beta_1 = 7.20 - 1.44\,\sigma.$$

The goodness of this correlation can be judged from the value of the correlation coefficient, r, of 0.955. This observed linear correlation indicates that the mode of chelation between Cu(II) and the ligand does not vary with the substituent; otherwise irregularities would have resulted. Again, the negative value of the reaction constant, *i.e.*, the slope of the plot, can only mean that the reaction studied is favored by electron donation to the metal. This explanation is further supported by plotting the so-called stabilization factor, S_f,[21] defined by the equation:

$$S_f = \log\,(\beta_1/K_1)_X - \log\,(\beta_1/K_1) = \rho\sigma$$

versus σ. As shown in Fig. 4, the plot is linear with a nagative slope; $S_f = -2.124\,\sigma$. This result is contrary to what has been reported for Cu(II) complexes of substituted benzoic acids, and for pyridine adducts of Cu(II) acetylacetonates.[21,22] Accordingly, it is not unreasonable to conclude that the explanation of the stabilization of Cu(II) complexes, based on the back donation of electrons from the metal to the ligand, does not seem likely in the Cu(II)–benzoylacetanilide chelates. This conclusion is also in agreement with the recently reported[3] spectral characteristics of the solid benzoylacetanilide complexes of copper(II).

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