Substituent Effects on the Stability Constants of Chelates of Some Trivalent Lanthanide Ions with Benzoylacetarylamides

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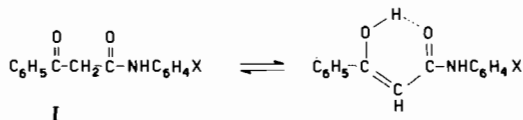
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Received March 31, 1977

Acid dissociation constants of nine benzoyl-acetarylamides have been determined potentiometrically in 70 vol.% ethanol–water at 30 °C. The stability constants of their 1:1 chelates formed with six trivalent lanthanide ions have also been determined. The effects of substituents in the ketoanilide on the equilibria are discussed.

Introduction

There has been appreciable interest in the lanthanide(III) complexes with various organic ligands [1, 2]. However, there has been apparently no systematic investigation of substituent effects on the stability of such metal chelates. This paper reports the results of a potentiometric study of the acid dissociation constants of a series of benzoylacetarylamides (Ia to Ii) and the stability constants of the 1:1 complexes formed between each of these ligands and Pr(III), Nd(III), Sm(III), Gd(III), Dy(III), and Er(III) in 70 vol.% ethanol–water solution at 30.0 ± 0.1 °C. The ligands Ia to Ii have found use as intermediates in the color photographic process [3] and are capable of keto–enol tautomerism which results in the formation of six-membered chelate ring (Scheme 1) [4, 5]. No data have been yet reported on complex formation between such ligands and the trivalent rare earth ions.

$$C_6H_5\ \overset{O}{\underset{\|}{C}}-CH_2-\overset{O}{\underset{\|}{C}}-NHC_6H_4X \quad \rightleftharpoons \quad C_6H_5-\underset{\underset{H}{C}}{C}\overset{\overset{H}{\cdot\cdot\cdot}}{\underset{}{O}}\ \ \overset{O}{\underset{\|}{C}}-NHC_6H_4X$$

I

a, X = 4-C₂H₅O   d, X = 3-CH₃O   g, X = 3-Br
b, X = 4-CH₃   e, X = 4-Br   h, X = 4-EtOOC
c, X = H   f, X = 3-Cl   i, X = 4-CH₃CO

Scheme 1.

The present investigation was undertaken to obtain quantitive information pertinent to the electronic effects on the stability of lanthanide(III) chelates caused by substituents on the *meta* and *para* positions of the benzene ring of the amide moiety of I. Due to the limited solubility of I and their metal chelates in aqueous media, measurements were carried out in 70 vol.% ethanol–water solution.

Experimental

The ligands Ia to Ii were synthesized by the method described [6] for benzoylacetanilide (Ic) employing the appropriately substituted aniline. The physical constants of the compounds prepared agreed with those in the literature [4–6]. A set of 0.10M solutions of the ligands were prepared in absolute ethanol. Ethanol–water (70% v/v) mixture was used in preparing potassium hydroxide (0.02M) and potassium nitrate (0.5M) solutions. Stock solutions of Ln(III) nitrates were prepared from the corresponding metal oxides (BDH AnalaR reagents, 99.9%) and the strength of each solution was determined by EDTA titration as previously described [7].

Measurements of pH were made using a Radiometer pH meter type 63 equipped with a combined glass electrode type GK 2311C. Autoburette type Metrohm Herisan Multi-Dosimat E415, accurate to ±0.01 ml was used.

The general procedure in the titration was as follows: 50 ml of a solution with a metal ion concentration of $2.0 \times 10^{-3}M$, a ligand concentration of $6.0 \times 10^{-3}M$, and KNO₃ in an amount to give the desired ionic strength (0.01 to 0.10) were transferred to 100 ml capacity water-jacketed cell which was thermostated at 30 ± 0.1 °C. The solution was then titrated by successive addition of 0.02 ml of potassium hydroxide solution. The pH of the solution was read after each addition of base and the lapse of sufficient time for attainment of equilibrium. The titration was continued until visual precipitation occurred. This usually happened at pH > 6.8. Typical titration curves are shown in Fig. 1. In all titrations a carbon dioxide free nitrogen atmosphere was maintained above the solution. All titrations were repeated at least twice and agreement between pH readings of the different titrations was usually within ±0.01.
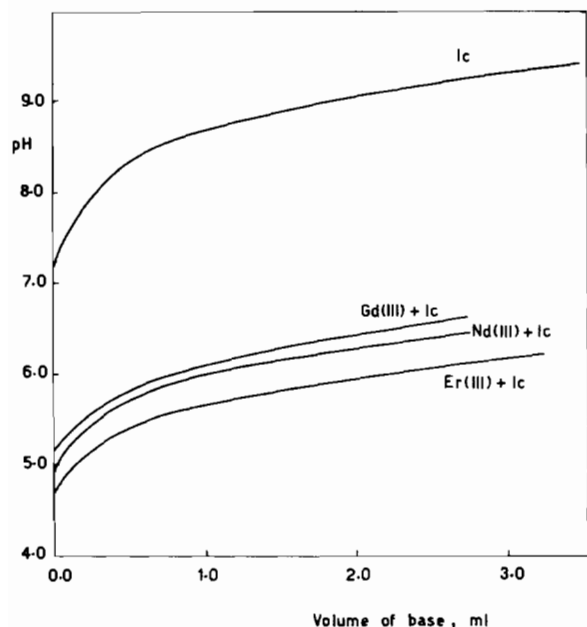
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Fig. 1. Potentiometric titration curves of benzoylacetanilide (Ic) in the absence and presence of metal ions in 70 vol.% ethanol–water and at μ 0.10 and 30 °C. [Ic] = 6.0 × $10^{-3}M$; [Gd(III)] = [Nd(III)] = [Er(III)] = 2 × $10^{-3}M$.

Results

The pH meter readings (B) in ethanol–water (70% v/v) medium were converted into hydrogen ion concentrations by means of eq. [1];

$$-\log[H^+] = B + \log U_H \qquad [1]$$

where $\log U_H$ is the correction factor at a given composition of the medium at a fixed temperature [8]. In the present work, the value of $\log U_H$ in 70 vol.% ethanol–water at 30 °C and ionic strength of 0.1 was determined and turned out to be 0.50 ± 0.01.

The stoichiometric acid dissociation constant, pK_a, of each ligand can be calculated from the pH data by eq. [2];

$$pK_a = B + \log U_H +$$
$$\log \frac{C_{HL} - [H^+] - C_{OH} + [HO^-]}{[H^+] + C_{OH} - [HO^-]} \qquad [2]$$

where C_{HL} and C_{OH} are the analytical concentrations of the ligand and the base added respectively. As the value of pK_w in 70% ethanol is ~17 [9], the values of $[H^+]$ and $[HO^-]$ are very small compared with the values of C_{OH} and C_{HL}. It follows that

$$pK_a = B + \log U_H + \log \frac{C_{HL} - C_{OH}}{C_{OH}} \qquad [3]$$

Using eq. [3], the values of pK_a's for the ligands Ia to Ii were thus computed. In all the calculations, the concentrations were corrected for the change in volume produced by the addition of potassium hydroxide solution. The average values of pK_a computed this way were reproducible to ±0.01–0.03 pK unit. The data are summarized in Table I.

The stoichiometric stability constants ($\log B_1$) of the 1:1 chelates were computed from the titration data using eq. [4].

$$\log B_1 = \log(\bar{n}/1 - \bar{n}) - \log[L^-] \qquad [4]$$

where $[L^-]$ represents the concentration of the carbanion-enolate of the ligand used, and $\bar{n}$ is the average number of ligand molecules bound to metal ion. The following equations [5] and [6] were used to calculate $[L^-]$ and $\bar{n}$ respectively.

$$[L^-] = \frac{K_a}{[H^+]} (C_{HL} - C_{OH} - [H^+] + [HO^-]) \qquad [5]$$

$$\bar{n} = (C_{HL} - [L^-]((([H^+]/K_a) + 1))/C_M \qquad [6]$$

TABLE I. Acid Dissociation Constants (pK_a) of Benzoylacetanilides and Stability Constants ($\log B_1$) of Their 1:1 Lanthanide Chelates (30.0 ± 0.1 °C, μ 0.10 KNO_3, 70 vol.% ethanol–water).

Ligand	σ_X	pK_a[a]	$\log B_1$[b]					
			Pr	Nd	Sm	Gd	Dy	Er
Ia	−0.24	9.53	5.29	5.59	5.53	5.48	6.02	6.15
Ib	−0.17	9.50		5.57				6.14
Ic	0.00	9.34	5.09	5.40	5.35	5.29	5.84	5.95
Id	0.05	9.22		5.32				5.88
Ie	0.23	9.01		5.05				5.55
If	0.37	8.91		5.04				5.53
Ig	0.39	8.95		4.96				5.48
Ih	0.45	8.83		4.88				5.45
Ii	0.50	8.72		4.81				5.40

[a] Standard deviation in pK_a, ±0.01–0.03. [b] Standard deviation in $\log B_1$, ±0.05.

where C_M is the metal ion concentration. The values of $\bar{n}$ were calculated from the pH data obtained before visual precipitation occurred. For all systems examined, values higher than 0.6 for $\bar{n}$ cannot be obtained, and thus the stability constant, B_1, for the 1:1 complex species only was calculated. The assumption of the presence of only 1:1 chelate over the experimental range proved correct as invariant values for the constant B_1 were obtained at different concentrations of the reactants. The values of $\log B_1$ determined are listed in Table I. The uncertainities in the numerical values of the formation constants, B_1, due to the possible hydrolysis of the central ion appear to be negligible over the experimental range. The linearity observed between $\log B_1$ values and pK_a or substituent σ_X constant confirmed *a posteriori* the correctness of this assumption.

For the determination of the thermodynamic acid dissociation and chelate stability constants, $p^T K_a$ and $\log^T B_1$ respectively, it is evident that

$$pK_a = p^T K_a - A\mu^{1/2} \qquad [7]$$

$$\log B_1 = \log^T B_1 - A'\mu^{1/2} \qquad [8]$$

where A and A' are constants and μ is the ionic strength of the medium at which the stoichiometric constants, pK_a and $\log B_1$, were determined. In the present investigation, the values of pK_a and $\log B_1$, determined at various μ, were plotted *versus* $\mu^{1/2}$, and the intercepts of the resulting plots (calculated by least squares method) were taken as values of $p^T K_a$ and $\log^T B_1$ respectively. The results are summarized in Tables II and III.

TABLE II. Values of pK_a for Benzoylacetanilide (Ic) at Different Ionic Strengths in 70 vol.% Ethanol–Water at 30.0 ± 0.1 °C.

$\mu \times 10^2$, KNO$_3$	0.25	1.00	2.25	5.00	10.00	15.00
$pK_a \pm 0.01$	9.79	9.72	9.64	9.50	9.34	9.21

TABLE III. Conditional and Thermodynamic Stability Constants for Ln(III) Chelates with Benzoylacetanilide Ic at 30 ± 0.1 °C in 70 vol.% Ethanol–Water.

Ln(III)	Pr	Nd	Sm	Gd	Er
$\log B_1{}^a$	5.09	5.40	5.35	5.29	5.95
$\log^T B_1$	5.87	6.19	6.16	6.07	6.76

[a]At μ 0.1, KNO$_3$.

Discussion

The pK_a values in Table I correspond to the apparent overall acid dissociation constants of the

keto and enol tautomers of the ligands investigated at μ of 0.1. In case of benzoylacetanilide (Ic), for example, the value of the thermodynamic acidity constant, $p^T K_a$, is 0.56 pK unit higher than that determined at μ of 0.1. The relation between the Hammett substituent constant σ_X and the pK_a values follows the equation:

$$pK_a = 9.299(\pm 0.016) - 1.065(\pm 0.053)\sigma_X \qquad [9]$$

with correlation coefficient $r = 0.991$. Comparison of the values of the reaction constants, defined by the slopes of the linear correlations, for the bases ArNHCOCHCOC$_6$H$_5$ and ArCOO$^-$ (1.065 and 1.74 [10] respectively) indicates that the NH link appears transmitting substituent effects with 61% efficiency, measured by the ratio: $\rho_{ArNHCO\overline{C}HCOC_6H_5}/\rho_{ArCOO^-}$ Our results for 70% ethanol–water solution of I can also be compared with those reported [12] for another series of I in aqueous solution containing <1% organic solvent, where ρ was found to have a value of 0.741. The low value of 0.741 observed for ρ in water is probably due to effects of the change in solvent. As the dielectric constant of the medium increases by decreasing the percentage of ethanol, there would be an increasing degree of charge stabilization by solvation of the carbanion-enolate. This results in lowering the susceptibility of the dissociation to substituent effects and thus the *rho* value decreases. This interpretation is also compatible with the finding of van Brandt *et al.* [11] that the acid dissociation constants of another series of benzoylacetarylamides in 60% ethanol–water follow the Hammett relation with $\rho = 0.790$.

The stability constants of Ln(III) chelates with the ligand Ia are linearly correlated with those with the ligand Ic. The equation of the regression line is expressed by eq. [10], [10] $\log B_1(\text{MIa}) = 1.001(\pm 0.013) \log B_1(\text{MIc}) - 0.201(\pm 0.075)$ with $r = 0.999$. The value of the intercept (−0.201) compares favourably with the difference between the pK_a values of the two ligands Ia and Ic used ($\Delta pK_a = -0.19$). The data effectively validate the application of eq. [11] when structurally similar ligands are compared [13].

$$\log B_1(\text{ML}) = \log B_1(\text{ML}') + (pK_a(\text{HL}') - pK_a(\text{HL})) \qquad [11]$$

The plot of $\log B_1$ for Nd(III) chelates *versus* $\log B_1$ for Er(III) was also linear and follows the equation:

$$\log B_1(\text{Nd}) = 0.968(\pm 0.041) \log B_1(\text{Er}) - 0.363(\pm 0.235) \qquad [12]$$

with $r = 0.995$. This result is adequately in agreement with the views of Irving and Rossotti [13] concerning the linear relationship between the complex stability constants of two metal ions with a related series of ligands.

As the relation between the metal ion and the ligand is regarded as a Lewis acid–base reaction, the correlation between the values of pK_a for the ligands Ia and Ii and the stoichiometric stability constants of their chelates with Nd(III), as a typical example of the series, was examined. The use of the conditional equilibrium constants (pK_a and $logB_1$) rather than the thermodynamic equilibrium constants (p^TK_a and log^TB_1) in such a correlation can be justified as follows. The relation between the p^TK_a of a series of ligands and log^TB_1 of their 1:1 metal chelates has been shown [14] to be

$$log^TB_1 = bp^TK_a + log^TB_{1o} - bp^TK_{ao} \qquad [13]$$

where o refers to the unsubstituted ligand. In terms of the conditional equilibrium constants, the latter relation becomes

$$logB_1 = bpK_a + (logB_{1o} - bpK_{ao} + (bY_{H^+} - Y_M)) \qquad [14]$$

where

$$Y_{H^+} = log(f_L/f_{Lo}) + log(f_{HLo}/f_{HL})$$

and

$$Y_M = log(f_{Lo}/f_L) + log(f_{ML}/f_{MLo})$$

In the above equations b is a constant and the f_i term refers to the activity coefficient of the species i. Under the conditions of constant temperature, ionic strength and solvent composition for determination of both pK_a and $logB_1$ for a series of related ligands, it may be assumed [14] that $f_{Lo} \simeq f_L$ and $f_{ML} \simeq f_{MLo}$, so that the Y_M term is close to zero. The same argument applies to the Y_{H^+} term. Consequently the term $(bY_{H^+} - Y_M)$ should be relatively small along the series, so that equation [14] becomes,

$$logB_1 = bpK_a + (logB_{1o} - bpK_{ao}) \qquad [15]$$

The $logB_1$ values for Nd(III) chelates with Ia to Ii, when plotted versus the pK_a values of the ligands, gave a straight line (Fig. 2) that follows closely the equation:

$$logB_1 = 0.993(\pm0.045)pK_a - 3.87(\pm0.410);$$
$$r = 0.993 \qquad [16]$$

Similarly, values of $logB_1$ for Er(III) chelates with the same series of ligands were linearly correlated with the pK_a values of such ligands (Fig. 2). The relation can be expressed by eq. [17].

$$logB_1 = 1.019(\pm0.061)pK_a - 3.566(\pm0.560);$$
$$r = 0.988 \qquad [17]$$

These observed linear relationship imply that the stability of lanthanide chelates is governed by the acidity of the ligands used. The values of the intercepts in eqs. [16] and [17] are in good agree-
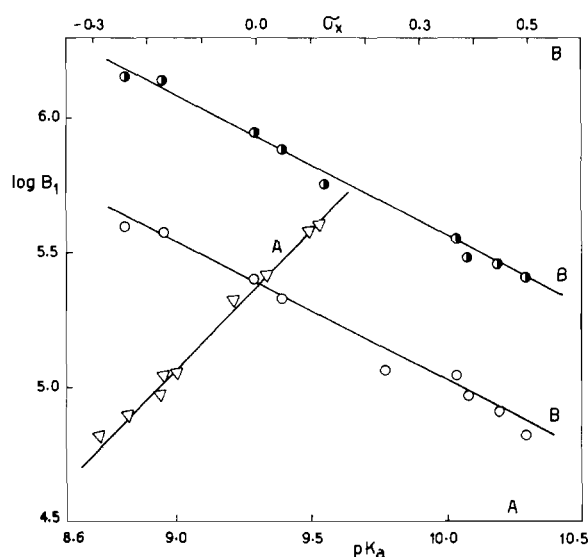

Figure 2. Dependence of $logB_1$ for Ln(III) chelates on the pK_a of the ligands and Hammett substituent constant, σ_X. $\triangle$ and $\bigcirc$ Nd(III) chelates. $\bigcirc$ Er(III) chelates.

ment with the respective values of the term ($logB_{1o}$ − bpK_{ao}) of eq. [15]. This agreement substantiates the foregoing assumption that the value of the term (bY_{H^+} − Y_M) is close to zero. Furthermore, the observation of the slopes of unity for the relations of eqs. [9], [11], and [16] suggests that the free energy of the displacement reaction: $M_1L + M_2 = M_2L + M_1$, is independent of the ligand (eqs. [11] and [16]), and that of $ML_1 + L_2 = ML_2 + L_1$ independent of the metal ion (eq. [9]). Such a behaviour is characteristic of the so called "structural" substituent effect [14]. The mutual dependence of the slopes of the plots of $logB_1(ML)$ versus $logB_1(M_oL)$ and of $logB_1(ML)$ against $logB_1(MLo)$ on the particular metal ions and ligands compared respectively is considered as a "normal" substituent effect [14].

Next the applicability of the Hammett equation to the $logB_1$ values for the chelates of Er(III) and Nd(III), as typical examples, was examined. In both cases, plots of $logB_1$ versus the substituent constant σ_X, were linear (Fig. 2). The equations of the regression lines obtained are:

$$logB_1(Er) = 5.916(\pm0.021) - 1.089(\pm0.066)\sigma_X;$$
$$r = 0.987 \qquad [18]$$

$$logB_1(Nd) = 5.367(\pm0.017) - 1.064(\pm0.055)\sigma_X;$$
$$r = 0.991 \qquad [19]$$

The negative slopes of these Hammett relations indicate that complexing of Ln(III) with the ligands Ia to Ii is favoured by electron releasing substituents that increase the electron density on the coordination sites of the ligand molecule. Moreover, the similarity between the values of slopes of eqs. [9], [18] and

[19] suggests that the acid dissociation and chelation equilibria of the ligands Ia to Ii exhibit the same sensitivity to the effects of coplanarity, resonance, inductive and solvent interactions.

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