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Kinetics and Mechanism of the Reaction of Iron(III) with Some Benzoylacetanilides

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The kinetics of the reactions of iron(III) with benzoylacetanilides have been studied by stopped flow technique in the pH range 1.0—2.0 in water–ethanol media. The effect of temperature on the reaction rate was also studied. A mechanism was proposed to account for the observed kinetic date. Rate constants for the reaction of Fe(III) with eight different benzoylacetanilides were correlated by Hammett equation, log $k_X = -0.51\,\sigma_X - 0.98$.

Keywords——benzoylacetanilides; iron(III) complexes; kinetics; substituent effects; stability constant

In an earier report,[2] it was concluded that metal-ligand complexation usually follows a sequence of successive steps. For an *m*-dentate ligand interacting with iron (III), the following steps may take place,

$$(\mathrm{Fe(H_2O)_6})^{3+} + \mathrm{L}^{n-} \overset{\text{fast}}{\rightleftarrows} \mathrm{Fe(H_2O)_6L}^{(n-3)-} \overset{\text{slow}}{\rightleftarrows}$$

$$\underset{\text{monodentate complex}}{(\mathrm{Fe(H_2O)_5})\mathrm{L}^{(n-3)-}} + \mathrm{H_2O} \rightleftarrows \underset{m\text{-dentate complex}}{\mathrm{Fe(H_2O)}_{6-m}\mathrm{L}^{(n-3)-}} + m\mathrm{H_2O} \qquad (1)$$

Moreover, it was reported[3,4] that when the anions of strong acids react with $(\mathrm{Fe(H_2O)_6})^{3+}$, rates increase with decreasing $(\mathrm{H^+})$. This was explained in terms of increasing reactivity of $(\mathrm{Fe(H_2O)_5OH})^{2+}$ over $(\mathrm{Fe(H_2O)_6})^{3+}$ as pH increases. On the other hand, when anions of weak acids react, the rates decrease with decreasing $(\mathrm{H^+})$ in acid region.[5] The reaction was assumed to take place between $(\mathrm{Fe(H_2O)_6})^{3+}$ or $(\mathrm{Fe(H_2O)_5OH})^{2+}$ and the neutral acid, at least in part.

Benzoylacetarylamide (I) are useful photographic color intermediates.[6] Although much information is available in literature concerning the chelating properties of such compounds,[7] essentially none exists regarding the kinetics and mechanism of their reaction with metal cations. We wish now to report the results of the investigation of the kinetics of the formation of 1:1 complex of iron (III) with I. The object of such a study was on one hand, to elucidate the mechanism of the chelate formation and, on the other, to examine substituent effects on the reactivity of such ligands.

$$\mathrm{C_6H_5COCH_2CONHC_6H_4X}$$

I

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[1] Location: *State of Kuwait.*

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Experimental

Materials and Solutions——Benzoylacetarylamides (Ia—h) were prepared by the condensation of equimolar amounts of ethyl benzoylacetate and the appropriate aniline following the procedure of Brown.[7] The compounds were recrystallized from EtOH to constant melting point and kept *in vacuo*. Their physical constants agreed with those in literature.[7] Stock solutions of the ligands (5.0×10^{-2} M) and ferric chloride (1.0×10^{-3} M–0.10 M HCl) in ethanol were prepared. The concentration of iron(III) stock solution was determined by gravimetric method as Fe_2O_3.

The concentrations of benzoylacetarylamides used in the kinetic runs were in the range $(2.5—6.0) \times 10^{-3}$ M, while that of iron(III) was always 1.0×10^{-4} M. Concentrations less than that stated were used when the solubility of the ligand was low. The solutions of ligands and iron(III) were prepared separately by dilution of their respective solutions such that their final solvent composition and ionic strength (0.10 M) were constant. The concentrations of the ligands were always at least 25 times that of iron(III) ion.

A Radiometer pH meter accurate to ±0.01 pH unit, fitted with a combined glass electrode type GK 2310 C, was employed for determination of pH. It was calibrated using two standard Radiometer buffer solutions at pH's 4.01 and 7.00. The pH-meter readings (B) recorded in ethanol–water solutions were corrected to hydrogen ion concentrations (H^+) by means of the widely used relation of Van Uitert and Haas,[8] namely,

$$-\log(\mathrm{H}^+) = B + \log U_{\mathrm{H}} \qquad (2)$$

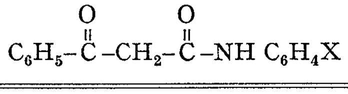
where $\log U_{\mathrm{H}}$ is the correction factor for the solvent composition and ionic strength for which B is read. For this purpose, readings were made on series of solutions containing known amount of HCl and KCl such that the ionic strength is equal to 0.10 M in 50, 60, and 70% by volume ethanol–water solutions at (25° ±0.1)°. The values of $-\log U_{\mathrm{H}}$ were found to be 0.25, 0.30 and 0.35, respectively.

A Durrum Stopped-flow spectrophotometer was used for the kinetic measurements. The observing chamber (of pathlength=20 mm) and mixing syringes were thermostated at the required temperature in the range 20—30° (±0.10). The wavelength used was 560 nm. It is important to mention that the 1:1 complex of benzoylacetarylamides with iron(III) absorb in the wavelength range 450—700 nm. In all runs, the reactions were followed to 80% completion.

Results and Discussion

In a previous report[9] two of the authors have shown that benzoylacetanilide I forms with iron (III) three mononuclear complexes in 60 vol. % ethanol-water medium in the pH range 1.0 to 11.0. An invariant stability constant was obtained at pH's $\leqslant 2$ when data were only interpreted in terms of the formation of 1:1 complex at wide range of metal ion and ligand concentrations. Table I depicts the acid dissociation constants, pK_a, of the ligands and the stability constants ($\log \beta_1$) of their 1:1 chelate complexes with iron (III).

TABLE I. The Dissociation Constants of Differently Substituted Benzoylacetarylamides (I) and Their 1:1 Iron (III) Complexes



$$C_6H_5-\overset{\overset{\Large O}{\|}}{C}-CH_2-\overset{\overset{\Large O}{\|}}{C}-NH\ C_6H_4X$$

Compound	X	PK_a	$\log \beta_1$	σ_X[a]
Ia	4-OC_2H_5	9.81	10.10	−0.30
Ib	4-OCH_3	9.81	10.10	−0.27
Ic	4-CH_3	9.61	9.91	−0.17
Id	3-CH_3	9.53	9.71	−0.07
Ie	H	9.43	9.52	0
If	3-Cl	9.15	9.07	+0.37
Ig	3-Br	9.11	8.90	+0.39
Ih	3-NO_2	8.76	8.41	+0.71

a) Hammett substituent constant.

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[8] L.G. van Uitert and C.G. Haas, *J. Am. Chem. Soc.*, **75**, 451 (1953).

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The reaction of iron (III) with I were followed spectrophotometrically by following the increase in the absorbance of the reaction mixture at the wavelength of 560 nm where maximum absorption difference between the reactants and the 1:1 chelate was observed. All kinetic runs were carried out under pseudo-first order conditions. The pseudo-first order rate constants, $k_{obs.}$, were obtained from the slopes of plots of log $(A_\infty - A_t)$ *vs.* time. The average deviation from the mean value of the rate constant in duplicate or triplicate experiments was ±5% or less.

For the reactions of iron (III) with all benzoylacetarylamides at a given pH, the following rate equation was obtained;

$$k_{obs.} = a + bT_{HL} \tag{3}$$

where a and b are constants and T_{HL} is the total ligand concentration. This is illustrated in Fig. 1, where a plot of k_{obs}. against T_{HL} gives a straight line. The values of the constants, a and b obtained at various pH's are given in Table II.

These data indicate that whereas "a" varies linearly with hydrogen ion concentration, the b values exhibits an inverse relation with (H^+), as shown in Figures 2 and 3, respectively. The equations of the straight lines in the latter Figures are:

TABLE II. Values of the Parameters a and b, eq. (1), at Different pH Values

pH	$a \times 10^2$ [a] (sec^{-1})	b[a] ($1\ mol^{-1}\ sec^{-1}$)
1.00	6.50	7.69
1.09	5.75	7.89
1.22	4.80	8.10
1.40	4.10	8.18
1.70	3.10	8·90

[a] The standard deviation is ± 0.01.

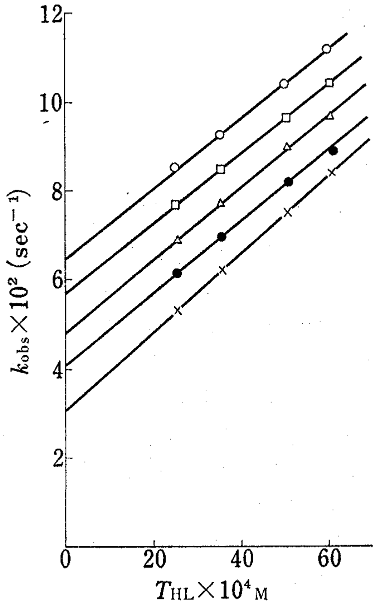


Fig. 1. Observed Rate Constant as Function of T_{HL}, (Ie), at Various pH's ($T_{Fe} = 1.0 \times 10^{-4}$M, μ= 0.01 M, T=20°, 60 vol% ethanol–water medium)

$[H^+] \times 10^2$M, ○: 10, □: 8, △: 6, ●: 4, ×: 2

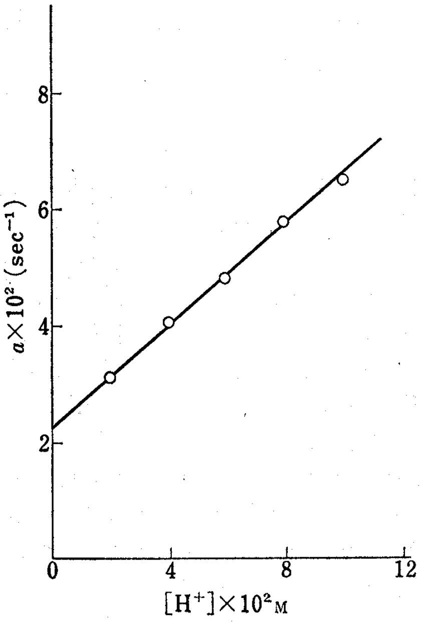


Fig. 2. Variation of a as Function of Hydrogen Ion Concentration

$$a = 2.25\times10^{-2} + 0.44(\mathrm{H}^+) \tag{4}$$

$$b = 7.60 + 2.53\times10^{-2}(\mathrm{H}^+)^{-1} \tag{5}$$

In order to account for the foregoing results, the reaction sequence presented in Scheme 1 is proposed. In this scheme, the chloro complexes of iron (III) other than 1:1 species are ignored. Moreover, the hydrolytic and/or polymeric species of iron (III) other than $\mathrm{Fe(H_2O)_5OH^{2+}}$ are neglected in the pH range 1.00—2.0 covered. Also, it is assumed that the vertical protolytic reactions in this scheme are at equilibrium owing to the fact they are very fast in comparison with that of complex formation. Furthermore, since the dissociation constant of Ie is 3.72×10^{-10}, it was not unreasonable to ignore reactions (d), (e) and (f) in Scheme 1.

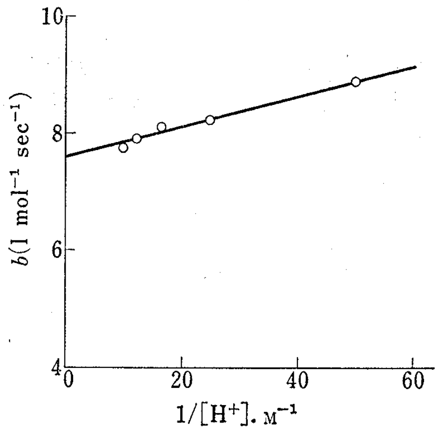
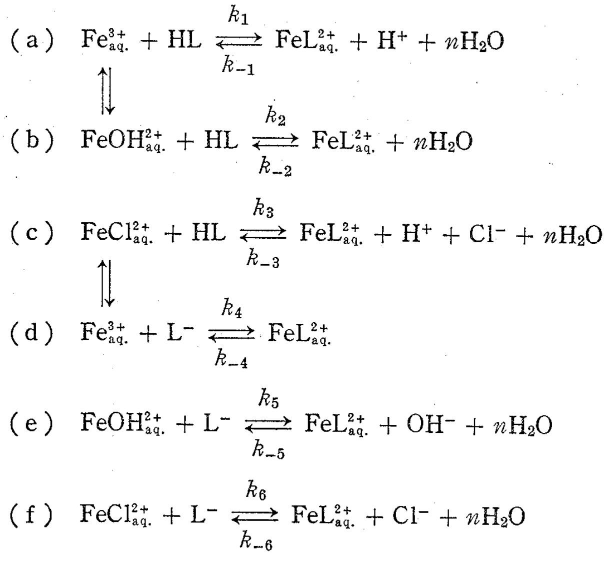


Fig. 3. Variation of b as Function of the Reciprocal of Hydrogen Ion Concentration

1/[M⁺]. M⁻¹



$$\text{(a)}\quad \mathrm{Fe^{3+}_{aq.} + HL \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} FeL^{2+}_{aq.} + H^+ + \mathit{n}H_2O}$$

$$\updownarrow$$

$$\text{(b)}\quad \mathrm{FeOH^{2+}_{aq.} + HL \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} FeL^{2+}_{aq.} + \mathit{n}H_2O}$$

$$\text{(c)}\quad \mathrm{FeCl^{2+}_{aq.} + HL \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} FeL^{2+}_{aq.} + H^+ + Cl^- + \mathit{n}H_2O}$$

$$\updownarrow$$

$$\text{(d)}\quad \mathrm{Fe^{3+}_{aq.} + L^- \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} FeL^{2+}_{aq.}}$$

$$\text{(e)}\quad \mathrm{FeOH^{2+}_{aq.} + L^- \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} FeL^{2+}_{aq.} + OH^- + \mathit{n}H_2O}$$

$$\text{(f)}\quad \mathrm{FeCl^{2+}_{aq.} + L^- \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} FeL^{2+}_{aq.} + Cl^- + \mathit{n}H_2O}$$

Scheme 1

Taking into account the foregoing assumptions, the rate equation describing the above sequence (a), (b) and (c) can thus be written as fololws:

$$\frac{d(\mathrm{FeL^{2+}})}{dt} = (\mathrm{Fe^{3+}})(\mathrm{HL})\{k_1+k_2K_{\mathrm{OH}}(\mathrm{H^+})^{-1}+k_3K_{\mathrm{Cl}}(\mathrm{Cl^-})\} - (\mathrm{FeL^{2+}})\{k_{-1}(\mathrm{H^+})+k_{-2}+k_{-3}(\mathrm{H^+})(\mathrm{Cl^-})\} \tag{6}$$

where Fe $\mathrm{L^{2+}}$ is the iron (III) complex species with HL, and K_{OH} and K_{Cl} are the hydrolysis constant of $\mathrm{Fe^{3+}}$ and the stability constant of its monochloro complex, respectively. The values of K_{OH} and K_{Cl} were not reported in 60 vol. % ethanol–water solution. However, approximate values of these constants may be obtained for reactions performed in aqueous ethanol solutions. The value of K_{OH} was in the range (2.25—4.00) 10^{-3} M depending on the temperature of the solution.[10] Regarding the values of K_{Cl}, it was reported[11] that they are of small magnitude. An approximate value of 0.11 was adopted at $\mu=0.1$ M. One should expect that the values of K_{OH} and K_{Cl} will slightly increase by decreasing the water content of the solvent mixture as the polarity of the latter would decrease. If we assume that the pH is not altered during the reaction progress, which is actually the case since $T_{\mathrm{HL}}\gg T_{\mathrm{M}}$ and the pH range is 1.00—2.0, the integrated form of equation 6 would be

$$\ln\frac{(\mathrm{FeL^{2+}})_\infty}{(\mathrm{FeL^{2+}})_\infty-(\mathrm{FeL^{2+}})_t} = kt \tag{7}$$

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where

$$k = k_{-1}(\mathrm{H}^+) + k_{-2} + k_{-3}(\mathrm{H}^+)(\mathrm{Cl}^-) + (\mathrm{HL})\frac{k_1+k_2K_{\mathrm{OH}}(\mathrm{H}^+)^{-1}+k_3K_{\mathrm{Cl}}(\mathrm{Cl}^-)}{1+K_{\mathrm{OH}}(\mathrm{H}^+)^{-1}+K_{\mathrm{Cl}}(\mathrm{Cl}^-)}$$

Since

$$\ln\frac{(\mathrm{FeL}^{2+})_\infty}{(\mathrm{FeL}^{2+})_\infty-(\mathrm{FeL}^{2+})_t} = \ln\frac{\mathrm{As}}{\mathrm{As}_\infty-\mathrm{As}_t} = k_{\mathrm{obs.}}t,$$

k can be correlated with $k_{\mathrm{obs.}}$. In the above equation As_∞ and As_t correspond to the absorbance values of the reaction mixture at infinite time and time t, respectively. Recalling equation 3, the parameter a can, accordingly, have the expression:

$$a = k_{-2} + (\mathrm{H}^+)\{k_{-1}+k_{-3}(\mathrm{Cl}^-)\} \tag{8}$$

Equating the latter expression (8) with equation (4) would yield

$$k_{-2} = 2.25\times10^{-2}\ \mathrm{sec}^{-1} \tag{9}$$

and

$$k_{-1} + k_{-3}(\mathrm{Cl}^-) = k_{-1} + k_{-3}(0.1) = 0.44\quad \mathrm{l\cdot mol^{-1}\cdot sec^{-1}} \tag{10}$$

Similarly, from equations 3 and 8

$$b = \frac{k_1+k_2K_{\mathrm{OH}}(\mathrm{H}^+)^{-1}+k_3K_{\mathrm{Cl}}(\mathrm{Cl}^-)}{1+K_{\mathrm{OH}}(\mathrm{H}^+)^{-1}+K_{\mathrm{Cl}}(\mathrm{Cl}^-)} \tag{11}$$

Comparing the latter with equation 5 indicates that,

$$1 + K_{\mathrm{OH}}(\mathrm{H}^+)^{-1} + K_{\mathrm{Cl}}(\mathrm{Cl}^-) \simeq 1 \tag{12}$$

Hence,

$$k_2K_{\mathrm{OH}} = 2.53\times10^{-2} \text{ and } k_2 \simeq 11.2\quad \mathrm{l\cdot mol^{-1}\cdot sec^{-1}} \tag{13}$$

Where

$$K_{\mathrm{OH}} \simeq 2.25\times10^{-3}$$

and

$$k_1 + k_3K_{\mathrm{Cl}}(\mathrm{Cl}^-) = k_1 + k_3K_{\mathrm{Cl}}(0.1) = 7.6\quad \mathrm{l\cdot mol^{-1}\cdot sec^{-1}} \tag{14}$$

The stability constant, β_1, of the formation of the Fe L^{2+} species can be calculated as follows

$$\beta_1 = \frac{k_2K_{\mathrm{OH}}}{k_{-2}K_{\mathrm{a}}} \tag{15}$$

Thus, by substituting the values of k_2K_{OH} and k_{-2} together with that of K_{a} of Ie, a value of 3.02×10^9 was obtained for β_1. This value is in good agreement with the value ($\beta_1=3.31\times10^9$) obtained previously from the equilibrium study,$^{9)}$ Table I.

The equilibrium constants corresponding to reaction (a) in Scheme 1 may be evaluated if one ignores the terms $k_3\ K_{\mathrm{Cl}}\ (\mathrm{Cl}^-)$ and $k_{-3}(\mathrm{Cl}^-)$ with respect to k_1 and k_{-1}. In such case $k_1/k_{-1}=17.3$ and $\beta_1=k_1/k_{-1}\ K_{\mathrm{a}}=4.59\times10^{10}$. On the other hand, if k_1 and k_{-1} are ignored with respect to $k_3K_{\mathrm{Cl}}\ (\mathrm{Cl}^-)$ and $k_{-3}(\mathrm{Cl}^-)$, the stability constant corresponding to reaction (c) in Scheme 1 will be equal to $17.3/K_{\mathrm{Cl}}$ and $\beta_1=4.59\times10^{10}$. This value is a factor of ten greater than that obtained from equilibrium studies indicating that the forementioned approximations are not quite valid and the rate constants k_1, k_{-1}, k_3 and k_{-3} cannot be well separated. The contribution of reactions (a) and (c) in Scheme 1 to the formation of the complex species cannot be ignored.

The variation of k_{obs} with temperature at different pH values and in 60 vol. % ethanol are shown graphically in Fig. 4. From the slopes of such plots, the energy of activation (E_{a}) was estimated. The value is equal to 12.5±0.5 kcal/mole. It is independent of the pH of the medium. The entropy of activation (ΔS^*) is accordingly equal to −25.2±1.5 *e.u.* This result is to be expected since free rotation about the single bonds in the ligand becomes restricted during the chelate ring formation. The negative entropy of activation reflects also a crowded transition state in the formation of the iron (III) complex with HL.

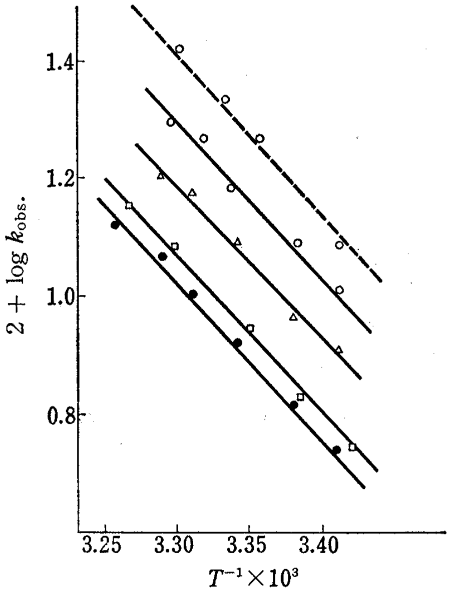

Fig. 4. Arrhenius Plot at Different pH Values

---○---, pH 0.95; ○, pH 0.95; △, pH 1.20; □, pH 1.70; ●, pH 2.05.
$[Fe^{3+}]$ 1×10^{-4} M. T_{HL} ----: 50×10^{-4} M, ——: 35×10^{-4} M. 60 % (v/v) ethanol.

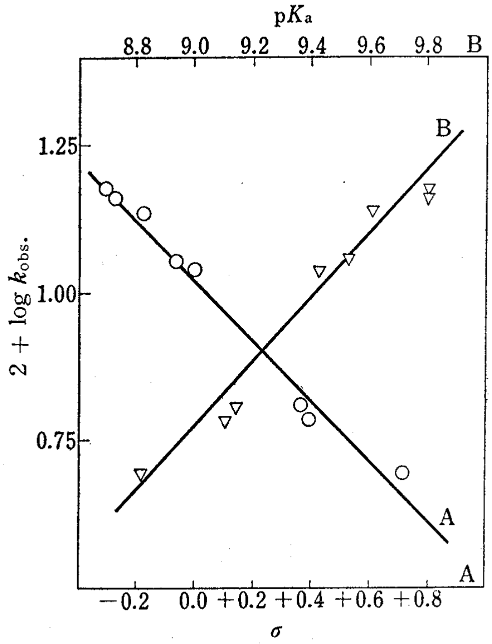

Fig. 5. Variation of log $k_{obs.}$ and pK_a as Function of σ_x

T: 30°. pH: 2.0. (Fe^{3+}) 5.0×10^{-5} M. T_{HL} 1.75×10^{-3} M. 60% (v/v) ethanol.

TABLE III. Pseudo First Order Rate Constants, $k_{obs.}$, at Different Solvent Compositions at 20°

$(Fe^{+3})=1.0\times10^{-4}$ M; $T_{HL}=3.5\times10^{-3}$ M
$(H^+)=0.1$ M $\mu=0.1$ M

% ethanol	$k_{obs.}\times10^2$ (sec.$^{-1}$)
50	7.0
60	9.0
70	12.6

The effect of the change in the solvent composition on the observed rate constant was also studied. The results, Table III, indicate that the value of k_{obs} increases as the ethanol percentage in the solvent increases. This finding seems to be compatible with the presumption that reaction (b) in Scheme 2 is the prevailing reaction. However, this dose not exclude entirely the contribution of reaction (c). In both cases, Fe OH^{2+} and Fe Cl^{2+} species will be more stable as ethanol percentage increases in the solvent mixture.

Next the effect of varying the substituents, on the anilide moiety of the ligand molecule, on the chelation rates was examined. For this purpose, the rates of the reaction of iron (III) with the anilides Ia to I_k were determined under identical conditions. In Figure 5, the values of log k_{obs} are plotted varsus the acid dissociation constants, pKa. As shown, the log k_{obs} is linearly related to pKa value. This implies that the formation of the FeL^{2+} species is dependent upon the basicity of the ligand. Figure 5 illustrates the resulting linear relation between log $k_{obs.}$ and σ. The equation of the straight line obtained is

$$\log k_{obs.} = -(0.51\pm0.03)\sigma - (0.98\pm0.01) \qquad (16)$$

From the magnitude and the sign of the reaction constant thus obtained, it is evident that electron-donating substituents facilitate the chelation process whereas electron-withdrawing groups retard it. The low susceptibility of the chelation process to substituent effects as indicated by the value of the reaction constant −0.51 can be attributed to the fact that the influence of the substituent on k_{forward} and $k_{\text{rev.}}$ change differently with σ.

As the formation constant β_1 of benzoylacetanilide-Fe (III) complex was shown to be given by relation (15), the overall reaction constant, ρ_1, for the formation of this 1:1 complex species will be given by

$$\rho_1 = \rho_2 - \rho_{-2} - \rho_a \qquad (17)$$

where ρ_2, ρ_{-2} and ρ_a are the reaction constants for the chelate formation, chelate decomposition, and the acid dissociation of the ligand respectively. Substituting the values −1.693, −0.51 and +0.933 of ρ_1, ρ_2 and ρ_a respectively in equation (17) would yield a value of +0.257 for the reaction constant, ρ_{-2}, of the dissociation of the 1:1 chelate species. As expected the process of the dissociation of the complex is favoured by electron-withdrawing substituents.

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Acylation of 2-Cyanomethylbenzimidazole

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An acylation of 2-cyanomethylbenzimidazole (**2**), which has the NH and the active methylene group as active site, in acetone by the Schotten-Baumann method was carried out. The acylation occurred at the nitrogen of the imidazole ring when **2**, itself, was used as a base. In these experiments, **2** was condensed with acetone to give 2-(1-cyano-2-methyl-1-propenyl)benzimidazole (**4a**) in the presence of trimethylamine as a base, however, **2** could not react with acetone in the presence of pyridine as a base.

Keywords——acylation; 2-cyanomethylbenzimidazole; Schotten–Baumann method; basicity; active methylene

The chemistry of benzodiazepine series has extensively been studied.[2] Recently, we have synthesized 4-amino-1*H*-1,5-benzodiazepine-3-carbonitrile hydrochloride (**1**) by the reaction of *o*-phenylenediamine with ethoxymethylenemalononitrile.[3] The ring transformations of **1** were reported[4] and one of them afforded 2-cyanomethylbenzimidazole[5] (**2**). This paper deals with some interesting reactions, especially acylation of **2**, which was found during studies on structural determination of products obtained from the transformation of **1**.

Compound **2** did not dissolve in water, so that acylation of **2** by the Schotten-Baumann method was tried in acetone. The above experiment in the presence of pyridine as a base did not give an acylated compound but gave the hydrochloride **3**, unexpectedly. On the other hand, when trimethylamine (40% in water) was employed as a base, the free base **2** reacted with the solvent to give only 2-(1-cyano-2-methyl-1-propenyl)benzimidazole (**4a**). This result should be due to the reaction of the carbonyl group in acetone with the active methylene group in **2**. In these experiments, pyridine acts as a catalyst for hydrolysis of

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