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Rate of Complex Formation of Iron(III) with Several β-Diketones in Aqueous Perchlorate Solutions Determined by Solvent Extraction Method

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The rate of formation of iron(III) complexes with several β-diketones (HA) in aqueous sodium perchlorate solutions has been determined by a solvent-extraction method. The rate was found to be first order with respect to the reagent, and zero to an inverse second order with respect to the hydrogen-ion. From the results, the controlling step has been determined to be the formation of the first complex in aqueous solutions. Three types of unit reactions are suggested for this; (i) $Fe^{3+}+HA_{enol}$, which has an associative character; (ii) $Fe(OH)^{2+}+HA_{enol}$ and; (iii) $Fe(OH)^{2+}+A^-$, both of which has a dissociative character.

In previous studies,[1,2] the rate of complex formation of iron(III) with trifluoroacetylacetone (1,1,1-trifluoro-2,4-pentanedione, Htfa) in aqueous solutions was determined from kinetic data regarding solvent extraction in conjunction with equilibrium data of the complexes in a liquid–liquid system. In the present study, the rate of solvent extraction of iron(III) in aqueous 4 mol dm^{-3} sodium perchlorate solutions with several β-diketones (HA) was measured and the rates of complex formations with the reagents were calculated. Then, the effect of a nucleophilic tendency of the β-diketones on the reaction mechanism was considered. The results are compared with those from previous studies with trifluoroacetylacetone and 2-thenoyltrifluoroacetone (1-(2-thienyl-)-4,4,4-trifluoro-1,3-butanedione, Htta)[1-4] and with other β-diketones.[5]

Experimental

All the experiments were carried out at 298 K in a manner similar to that described in previous papers.[1,2,4] The β-diketones used were: acetylacetone (2,4-pentanedione, Hacac), benzoylacetone (1-phenyl-1,3-butanedione, Hbza), dibenzoylmethane (1,3-diphenyl-1,3-propanedione, Hdbm), benzoyltrifluoroacetone (1-phenyl-4,4,4-trifluoro-1,3-butanedione, Hbfa), and hexafluoroacetylacetone (1,1,1,5,5,5-hexafluoro-2,4-pentanedione, Hhfa). They were obtained from Dojindo Co., Kumamoto, Japan (Hacac, Hbfa, and Hhfa), Tokyo Kasei Co., Tokyo, Japan (Hbza), and Nakarai Chemicals Co., Kyoto, Japan (Hdbm). A portion of an aqueous 4 mol dm^{-3} (H,Na)ClO$_4$ solution containing iron(III) and an equal volume of carbon tetrachloride containing 5×10^{-5} to 1×10^{-3} mol dm^{-3} of one of the β-diketones were placed in a stoppered glass tube and agitated vigorously for a specific time interval and centrifuged. In some experiments, the two phases were agitated until a distribution equilibrium was established. The organic phase was washed by 4 mol dm^{-3} hydrochloric acid and any iron(III), thus back-extracted, was measured using an atomic absorption method. Any metal in an aqueous phase was also measured in a similar way. The hydrogen-ion concentrations in aqueous solutions were measured using potentiometry and a calibration curve which was obtained by measuring a set of standard perchloric acid solutions of the same ionic medium. Thus results were given in stoichiometric units. Spectrophotometric measurements were also made with acetylacetone complexes in order to determine their stability constants. An acid aqueous iron(III) solution and an aqueous Hacac solution were mixed and left standing until a complex formation equilibrium was reached. Then, the optical absorbance was measured at 440 nm to the reagent blank. The hydrogen-ion concentration was measured in a similar way.

Statistical

In this paper, the subscript "org" denotes a chemical species in an organic solution; a lack of it denotes species in an aqueous solution. An initial concentration is denoted by the subscript "init".

The acid-dissociation and two-phase distribution constant of a β-diketone and the stability constant of the "n-th" complex are defined as;

$$K_a = [H^+][A^-][HA]^{-1}, \tag{1}$$

$$K_d = [HA]_{org}[HA]^{-1}, \tag{2}$$

$$\beta_n = [FeA_n^{3-n}][Fe^{3+}]^{-1}[A^-]^{-n}. \tag{3}$$

The distribution ratio of metal ions when an equilibrium is established can be written as:

$$\begin{aligned} D &= [Fe(III)]_{org}[Fe(III)]^{-1} \\ &= [FeA_3]_{org}([Fe^{3+}]+\sum[FeA_n^{3-n}])^{-1} \\ &= K_{dm}\beta_3[A^-]^3(1+\sum\beta_n[A^-]^n)^{-1} \\ &= K_{ex}K_d{}^3K_a{}^{-3}[A^-]^3(1+\sum\beta_n[A^-]^n)^{-1}, \end{aligned} \tag{4}$$

where K_{dm} is the distribution constant of the tris-complex;

$$K_{dm} = [FeA_3]_{org}[FeA_3]^{-1}, \tag{5}$$

K_{ex} is the extraction constant defined by;

$$K_{ex} = [FeA_3]_{org}[H^+]^3[Fe^{3+}]^{-1}[HA]_{org}{}^{-3}. \tag{6}$$

From the initial concentration of HA, the hydrogen-ion concentration, and D at equilibrium, the values of β_n, K_{dm}, and K_{ex} can be obtained on the basis of Eq. 4 by a least-squares calculation.

The spectrophotometric data of the aqueous solutions obtained by the equilibrium study were treat-

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ed statistically as follows. Under the experimental conditions of the present work, the molar absorption coefficient of the hydrated Fe^{3+} species is negligible and, thus, the optical absorbance can be written as;

$$E = \sum\varepsilon_n[FeA_n^{3-n}]$$
$$= [Fe^{3+}]_{init} \times \sum\varepsilon_n\beta_n[A^-]^n \times (1+\sum\beta_n[A^-]^n)^{-1}, \quad (7)$$

where ε_n is the molar absorption coefficient of the "n-th" complex. From the initial concentration of HA, the hydrogen-ion concentration and E at equilibrium, β_n and ε_n can be calculated on the basis of Eq. 7.

The constant regarding the hydrolysis of Fe^{3+}, K_h, and that for the keto-enol tautomerism of a β-diketone, K_e, which are used for an analysis of the kinetic data are defined as;

$$K_h = [Fe(OH)^{2+}][H^+][Fe^{3+}]^{-1}, \quad (8)$$

$$K_e = [HA]_{enol}[HA]_{keto}^{-1}. \quad (9)$$

When the rate of complex formation is first order with respect to Fe^{3+} and when the controlling step is the formation of the first complex, the rate can be written as;

$$V = -\,d[Fe^{3+}]/dt = k_{obsd}[Fe^{3+}]. \quad (10)$$

The concentration of the unreacted Fe^{3+} at a certain time after the start of two-phase agitation can be calculated from the initial concentration of Fe^{3+} and that of extracted species using the following equation;[2)]

$$[Fe^{3+}] = [Fe^{3+}]_{init} - ((\beta_1\beta_3^{-1}[A^-]^{-2}+\beta_2\beta_3^{-1}[A^-]^{-1}+1)$$
$$\times K_{dm}^{-1}+1) \times [FeA_3]_{org}. \quad (11)$$

Results

Equilibrium Experiments. Since the solvent extraction of iron(III) with the β-diketones proceeded rather slowly, two-phase agitation was continued for 1 h (when Hacac or Hhfa was the extractant) or for 24 h (when Hbza, Hdbm, or Hbfa was the extractant) in order to establish equilibrium. Figure 1 shows a plot of log D *vs.* log $[A^-]$ at equilibrium. The equilibrium constants in Eqs. 3, 5, and 6 were calculated from these data on the basis of Eq. 4 using a least-squares program. The values of β_n and K_{dm}, thus obtained, were somewhat erroneous since the distribution ratio of iron(III) was too high under these conditions. The relative concentrations of the aqueous complexes were too high and the extractability of the tris(β-diketonato) complexes was also too high (K_{dm} was great) to allow an accurate determination of the equilibrium constants. On the other hand, the extraction constant, K_{ex}, could be determined much more accurately. The values of the obtained constants are listed in Table 1.

Figure 2 gives the absorbance of the solutions, normalized to an iron(III) concentration as a function of the ligand anion concentration. By analysing these data on the basis of Eq. 7, β_n and ε_n were obtained (Table 1).

Rate of Complex Formation in Aqueous Solutions. It was reported in a previous paper[9)] that a transient maximum appeared in the extraction of copper(II) with several β-diketones. This was explained in terms of the rate of the ketonization of the enol form β-diketones in an aqueous phase being rather low. The same type of transient maximum for extraction was observed with Hhfa in the present study. For this reason, a carbon tetrachloride solution of Hhfa was agitated with an

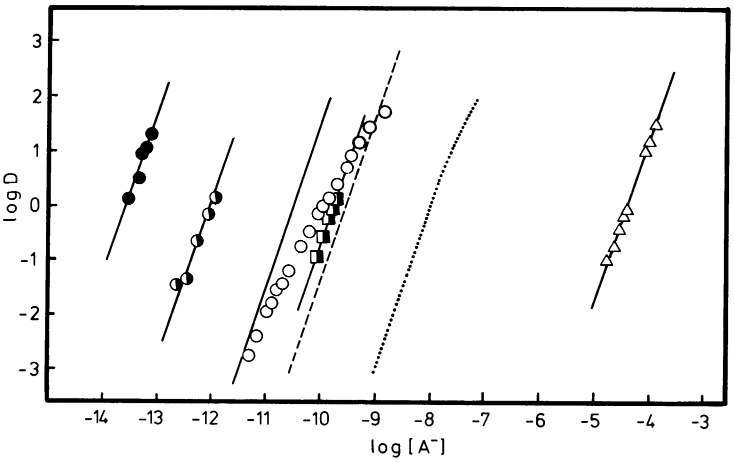

Fig. 1. Extraction curves of iron(III) with acac⁻ (○), bza⁻ (◑), dbm⁻ (●), bfa⁻ (◧), and hfa⁻ (△) as a function of ligand concentration into carbon tetrachloride. The solid lines show the slope of +3 which are calculated by introducing the values of K_{ex} in Table 1 into Eq. 4. The dotted and broken lines give the extraction curves of tfa⁻ and tta⁻ complexes in Refs. 1 and 3.

TABLE 1. EQUILIBRIUM CONSTANTS FOR SEVEN β-DIKETONES AND THEIR IRON(III) COMPLEXES

(a) Equilibrium constants for reagents	Hacac	Hbza	Hdbm	Htfa	Hbfa	Htta	Hhfa
log K_a	−10.1[6]	−9.2[5]	−9.3	−6.6[1]	−6.2[5]	−6.6[5]	−4.5
log K_d	0.2[5]	2.7[5]	5.0	0.4[1]	2.8[5]	1.9[5]	−1.0
log K_e	−0.6[7]	−0.4[8]	(−0.4)*	−2.0[8]	−1.8[8]	−1.8[8]	−3.3[9]

(b) Equilibrium constants for iron(III) complexes	Hacac§	Hbza	Hdbm	Htfa[1]	Hbfa	Htta	Hhfa
log β_1	11.4	(11.4)*	(11.4)*	6.7	(7.7)*	(7.7)*	2.7
	11.4†			7.7†			
log β_2	20.7	(20.8)*	(20.8)*	14.5	(14.4)*	(14.4)*	6.8
	20.8†			14.4†			
log β_3	—	(26.7)*	(26.7)*	20.3	(19.8)*	(19.8)*	9.8
	26.7†			19.8†			
log K_{dm}	4.7	(9.3)**	(14.2)**	4.2	(9.5)**	(9.7)**	3.6
log K_{ex}	0.5	0.3	−2.1	3.1	2.3	4.0[3]	2.7

Hydrolysis constant of iron(III). log K_h=−3.1 (Ref. 10.) † Determined by spectrophotometric method. * Estimated values. ** Calculated from K_{ex}, β_3, K_a, and K_d. § The stability constants of acetylacetonato complexes agree with literature values (Refs. 11, 12.) The molar absorption coefficients of acetylacetonato complexes at 440 nm obtained are; ε_1=540, ε_2=1750, and ε_3=2880, respectively.

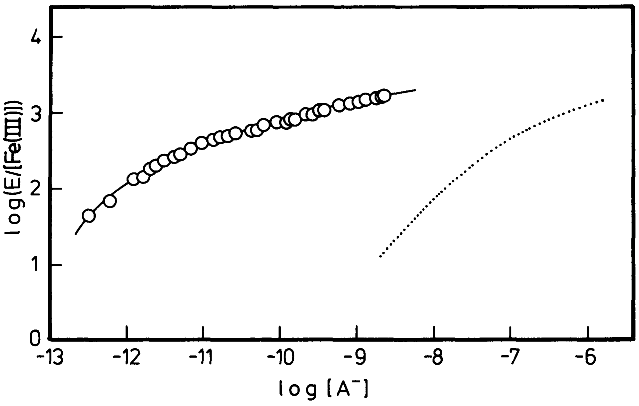

Fig. 2. Optical absorbance (normalized to the iron(III) concentration) of iron(III) complexes with acac⁻ (O) at 440 nm as a function of ligand concentration. The solid curve is calculated by introducing the constants in Table 1 into Eq. 7. The dotted line gives the results of tfa⁻ complexes at 450 nm in Ref. 1.

aqueous perchlorate solution containing no iron(III) for 10 min in order to establish the distribution and ketonization equilibria of the reagent. Then, iron(III) was added to the aqueous phase and kinetic measurements were initiated. The total amount of the iron(III) complexes formed was calculated from the amount of iron(III) extracted into an organic phase, by using Eq. 11. The rate of complex formation was found to be first order with respect to the reagent and zero to an inverse second order with respect to the hydrogen-ion. Figure 3 shows the dependence of the rate of complex formation to the β-diketone concentration; Fig. 4 gives the observed rate constants of the complex formation normalized to the β-diketone concentration in the aqueous phase as a function of the hydrogen-ion concentration. These results could be fitted to the following rate equation;

$$V = [\mathrm{Fe}^{3+}][\mathrm{HA}](k_\mathrm{A}+k_\mathrm{B}[\mathrm{H}^+]^{-1} + k_\mathrm{C}[\mathrm{H}^+]^{-2}). \tag{12}$$

The values of the rate constants k_A, k_B, and k_C were obtained by introducing data into Eq. 12 (Table 2). The rate of complex formation with Hacac was too high to determine the rate constant. This is because the solubility of the ligand in an aqueous phase is high and/or the proportion of the enol from to the total amount of reagent in an aqueous phase is also high.

Discussion

In the present study, the ionic concentration in an

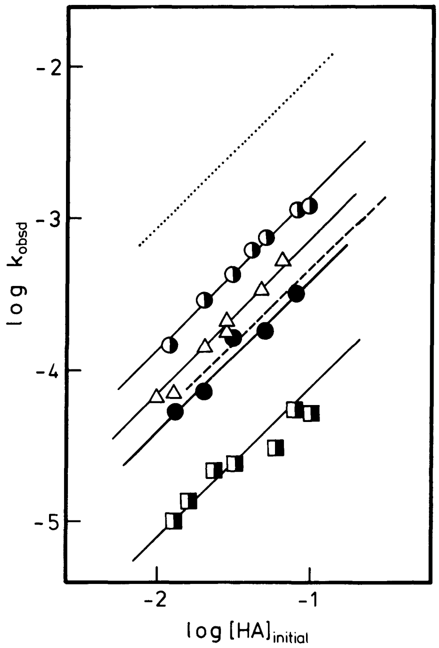

Fig. 3. Dependence of the rate of formation of iron(III) complexes with Hbza (◑), Hdbm (●), Hbfa (◨), and Hhfa (△) on the initial concentration of the reagents. The solid lines show the slope of +1. The dotted and broken lines give the results with Htfa and Htta in Refs. 2 and 4.

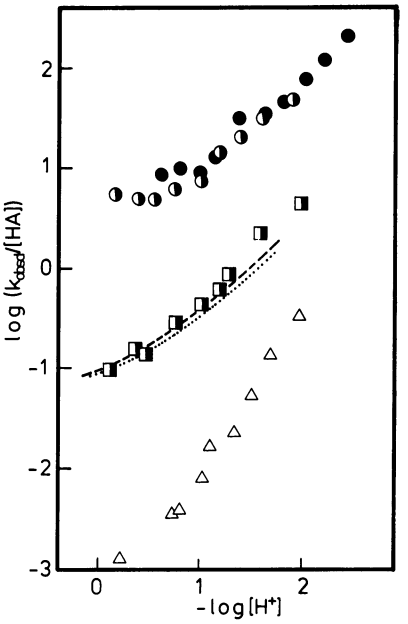

Fig. 4. Dependence of the rate of formation of iron(III) complexes (normalized to the β-diketone concentration in the aqueous phase) with Hbza (◑), Hdbm (●), Hbfa (◨), and Hhfa (△) on the hydrogen-ion concentration. The dotted and broken lines show the results with Htfa and Htta in Refs. 2 and 4.

aqueous phase was kept rather high in order to maintain the activity coefficient of the solutes constant even when for the great charge in the hydrogen-ion concentration was changed. However, the values of the stability constants for acetylacetonato complexes were not very much different from the literature at various ionic concentrations.[11,12]

The stability constants of the iron(III) complexes with bza$^-$, dbm$^-$, bfa$^-$, and tta$^-$ could not be obtained for the reason already mentioned above. However, it can be reasonably assumed that the values of β_n for the bza$^-$ and dbm$^-$ complexes are similar to those of the acac$^-$ complexes, and those of the bfa$^-$ and tta$^-$ complexes to that of the tfa$^-$ complex. In the present work, the estimated values of the stability constants of these four β-diketonato complexes on the basis of this assumption were used for an analysis of the kinetic data.

Since the data fit well with Eq. 12, it is assumed that the following reaction routes are possible.

k_A path:

$$Fe^{3+} + HA_{(enol)} \longrightarrow FeA^{2+} + H^+. \qquad (13)$$

k_B path:

$$Fe^{3+} + A^- \longrightarrow FeA^{2+}, \qquad (14)$$

and/or

$$[Fe(OH)]^{2+} + HA_{(enol)} \longrightarrow FeA^{2+} + H_2O. \qquad (15)$$

k_C path:

$$[Fe(OH)]^{2+} + A^- \longrightarrow FeA^{2+} + OH^-, \qquad (16)$$

and/or

$$[Fe(OH)_2]^+ + HA_{(enol)} \longrightarrow [FeA(OH)]^+ + H_2O. \qquad (17)$$

Because of the proton ambiguity, two possible reactions are given for both of the k_B and k_C paths. However, from the magnitudes of the rate constants for complex formations, the hydrolysis constant of iron(III), the equilibrium constant for the keto–enol tautomerism, and the acid-dissociation constant of the β-diketone, it was concluded that the route in Eq. 15 was more reasonable except when the reagent was Hhfa. Since the value of K_e of Hhfa, $[Hhfa]_{enol}/[Hhfa]_{keto}$, is much smaller and the acid-dissociation constant is larger than for other β-diketones, the concentration of the ligand, $[A^-]$, in an aqueous phase with this reagent under experimental conditions should be much higher than for the other β-diketones and both the reactions in Eqs. 14 and 15 could be possible. For the k_C path, the reaction in Eq. 16 was determined to be more reasonable since the second hydrolysis constant of Fe^{3+} is very small and, thus, the amount of the $[Fe(OH)_2]^+$ species should be extremely small under the present experimental conditions.

By using K_h of iron(III), K_a and K_e of the β-diketone and k_A, k_B, and k_C in Eq. 12, the rate of each controlling reaction can be written as;

$$\begin{aligned} V_0 &= k_0[Fe^{3+}][HA]_{enol} \\ &= k_A \times K_e^{-1} \times (1+K_e)[Fe^{3+}][HA], \qquad (18) \end{aligned}$$

$$\begin{aligned} V_1 &= k_1[Fe(OH)^{2+}][HA]_{enol} \\ &= k_B \times K_h^{-1} \times (1+K_e) \times K_e^{-1}[Fe^{3+}][HA][H^+]^{-1}, \qquad (19) \end{aligned}$$

$$V_1' = k_1'[Fe^{3+}][A^-] = k_B \times K_a^{-1}[Fe^{3+}][HA][H^+]^{-1}, \qquad (20)$$

$$\begin{aligned} V_2 &= k_2[Fe(OH)^{2+}][A^-] \\ &= k_C \times K_h^{-1} \times K_a^{-1}[Fe^{3+}][HA][H^+]^{-2}. \qquad (21) \end{aligned}$$

k_0, k_1, k_1', and k_2 were calculated using the above constants (Tables 1 and 2) using Eqs. 18 to 21. They are listed in Table 3.

TABLE 2. SUMMARY OF RATE CONSTANTS OBTAINED

	Hacac†	Hbza	Hdbm	Htfa[2]	Hbfa	Htta[4]	Hhfa
log (k_A/mol^{-1}dm^{3}s^{-1})	—	0.5	0.5	−1.2	−1.4	−1.2	−3.1
log (k_B/s^{-1})	—	−0.2	−0.2	−1.6	−1.4	−1.5	−3.3
log (k_C/mol dm^{-3}s^{-1})	—	—	—	—	—	—	−4.4

† Too fast to determine.

TABLE 3. RATE CONSTANTS FOR COMPLEX FORMATION OF IRON(III) IN AQUEOUS PERCHLORATE SOLUTIONS AT 298 K

	Hacac†	Hbza	Hdbm	Htfa[2]	Hbfa	Htta[4]	Hhfa*
log (k_0/mol^{-1} dm^3 s^{-1})	—	1.0	1.0	0.8	0.4	0.6	0.2
log (k_1/mol^{-1} dm^3 s^{-1})	—	3.4	3.4	3.5	3.5	3.4	3.1
log (k_2/mol^{-1} dm^3 s^{-1})	—	—	—	—	—	—	3.2

* The rate constant k_1' for the reaction in Eq. 20 is; log (k_1'/mol^{-1} dm^3 s^{-1})=1.2. † Too fast to determine.

Ishihara, Funahashi, and Tanaka reported that the rate constant and the activation volume for the formation of iron(III) complexes in aqueous solutions with 4-isopropyltropolone, thiocyanate ion, and acetohydroxamic acid.[13,14] They concluded that a reaction of hydrated Fe^{3+} proceeded in all cases by an associative interchange mechanism. That of $[Fe(OH)]^{2+}$ proceeded by a dissociative interchange mechanism. In the present study, the values of k_1 and k_2 (Eqs. 19 and 21) for the reaction of $[Fe(OH)]^{2+}$ are about $10^{3.4}$ with all the β-diketones. These agree well with the above reported values. For this reason, it was concluded that the k_B path could be more reasonably represented by Eq. 15 and the k_C path by Eq. 16. Moreover, the values of k_1 and k_2 agree well with the literature regarding $[Fe(OH)]^{2+}$ with several ligands. Since the mechanisms for these reactions were determined previous papers to be dissociative interchanges from the activation volumes, it should be reasonable to conclude here that the reactions described by Eqs. 15 and 16 also proceed by a mechanism which has a dissociative character.

In reactions of Fe^{3+}, the value of k_0 was greater when the reagent was a weaker acid. This indicates that the rate was higher when the nucleophilic tendency of the reagent was higher and consequently the mechanism should have an associative character. Thus, the mechanism of complex formation of iron(III) with these β-diketones is different when the metal species in the controlling reaction is Fe^{3+} and when it is $[Fe(OH)]^{2+}$.

As described in a previous paper,[2] equilibrium data for complexes formed from products of the controlling reaction are often indispensable in order to make a reasonable analysis of the kinetic data regarding solvent extraction. However, in most previous work regarding the rate of solvent extraction controlled by a complex formation in an aqueous phase, this has not been considered. For example, the rates of solvent extractions and complex formations of iron(III) with β-diketones (except Hdbm) were studied,[5] but no correction was made in the previous work regarding the effect of the complexes formed in the aqueous phase when the kinetic data were analyzed. As can be seen from the previous and present paper, somewhat different conclusions can be drawn from similar experimental data.

When both of the reagents and the complexes are relatively insoluble in water, as those in the present study, the solvent extraction method should be more useful than the spectrophotometric method of the aqueous solution provided that the product is extractable into organic solvents.

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