3260 © 1994 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 67, 3260—3262(1994) [Vol. 67, No. 12

Light and Shade Effect on the Synergistic Extraction of Iron(II) with 4,4,4-Trifluoro-1-(2-thienyl)-1,3-butanedione and Pyridine Base

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(Received May 26, 1994)

A synergistic extraction of iron(II) with 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione (TTA) and pyridine base was studied in order to clarify the effect of light and shade on the extraction. The extraction constant obtained at a shady place was larger than that obtained at a light place when pyridine or 4-methylpyridine was used as an additive. The stability constants for synergistic adducts at both places were almost the same, and hence it was concluded that the light and shade effect occurs in bonds between the central iron(II) and TTA anions.

Akaiwa et al. were the first to apply 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione (TTA=HR)–pyridine base (S) system to the spectrophotometric determination of iron(II). They showed that the iron(II)–TTA complex becomes stable by the addition of pyridine.[1] Thereafter, the composition of a synergistic adduct was shown to be FeR_2S_2, whose color caused by charge-transfer is reddish blue.[2] In the present work, it was found that the synergistic extraction constant for FeR_2S_2 obtained at a light place differs from that obtained by the extraction at a shady place.

Experimental

Apparatus. A Hitachi Model 100-60 spectrophotometer and a Hitachi Model 170-30 atomic absorption spectrometer equipped with iron hollow cathode lamp (Hamamatsu Photonics) were used. A Horiba Model F-80 pH analyzer and a Iwaki KM type shaker were also used.

Reagents. TTA and pyridine bases were obtained from Wako Pure Chemicals, and were used without further purification. Benzene and all the other chemicals used were of guaranteed grade. Deionized water was used throughout.

Extraction Procedure (1). Twenty cubic centimeters of an aqueous solution containing 2.00×10^{-4} mol dm^{-3} iron(II), 0.1 mol dm^{-3} sodium perchlorate and 1.5% hydroxylamine hydrochloride, whose pH was preliminarily adjusted by adding hydrochloric acid or sodium hydroxide, was placed in a separatory funnel. An equal volume of benzene solution containing 1.00×10^{-3} mol dm^{-3} TTA and 1.00×10^{-3} mol dm^{-3} pyridine base was added; the mixture was then shaken vigorously for 30 min in a light (fluorescent room lamp) or shaded place. After the phases were allowed to separate, the absorbance (E) of the organic phase at 580 nm was measured, and the pH of the aqueous phase was also measured. All experiments were carried out at room temperature (ca. 293 K). By using the absorbance (E_{100}) obtained at above 99% extraction, the distribution ratio of iron(II) was defined as follows:

$$D=\frac{E}{E_{100}-E}. \tag{1}$$

Extraction Procedure (2). Twenty cubic centimeters of an aqueous phase containing 2.00×10^{-4} mol dm^{-3} iron(II), 1.5% hydroxylamine hydrochloride and 0.1 mol dm^{-3} sodium acetate–acetic acid was placed in a separatory funnel. An equal volume of benzene solution containing 1.00×10^{-3} mol dm^{-3} TTA and pyridine base was added; the mixture was then shaken vigorously for 30 min in a light (fluorescent room lamp) or shaded place. After the phases were allowed to separate, iron(II) remaining in the aqueous phase was determined with the atomic absorption spectrometer, and the pH was also measured. All experiments were carried out at room temperature (ca. 293 K). The distribution ratio of iron(II) was defined as follows:

$$D=\frac{\text{The concentration of iron(II) in the } C_6H_6 \text{ phase}}{\text{The concentration of iron(II) in the } H_2O \text{ phase}}. \tag{2}$$

Results and Discussion

The total concentration of TTA can be written by Eq. 3, if the concentration of TTA combined with iron(II) can be neglected compared with that of free TTA:

$$\begin{aligned}[\mathrm{HR}]_{\mathrm{tot}} &= [\mathrm{HR}]_{\mathrm{org}}+[\mathrm{HR}]+[\mathrm{R}^-]\\ &= [\mathrm{HR}]_{\mathrm{org}}\left(1+\frac{1}{K_{\mathrm{DR}}}+\frac{K_{\mathrm{HR}}}{K_{\mathrm{DR}}[\mathrm{H}^+]}\right),\end{aligned} \tag{3}$$

where the subscript org denotes the organic phase, $K_{\mathrm{DR}}=[\mathrm{HR}]_{\mathrm{org}}[\mathrm{HR}]^{-1}$ and $K_{\mathrm{HR}}=[\mathrm{H}^+][\mathrm{R}^-][\mathrm{HR}]^{-1}$. By using $\log K_{\mathrm{DR}}=1.6$ and $\mathrm{p}K_{\mathrm{HR}}=6.23$,[3] Eq. 3 can be rewritten as

$$[\mathrm{HR}]_{\mathrm{tot}}=[\mathrm{HR}]_{\mathrm{org}}\left(1.03+\frac{1.48\times10^{-8}}{[\mathrm{H}^+]}\right). \tag{4}$$

Equation 4 enables us to calculated $[\mathrm{HR}]_{\mathrm{org}}$. By neglecting the concentration of pyridine base combined with iron(II), the total pyridine base concentration added to the extraction system is given by

$$\begin{aligned}[\mathrm{S}]_{\mathrm{tot}} &= [\mathrm{S}]_{\mathrm{org}}+[\mathrm{S}]+[\mathrm{HS}^+]\\ &= [\mathrm{S}]_{\mathrm{org}}\left(1+\frac{1}{K_{\mathrm{DS}}}+\frac{[\mathrm{H}^+]}{K_{\mathrm{DS}}K_{\mathrm{HS}}}\right)\\ &= [\mathrm{S}]_{\mathrm{org}}\alpha_{\mathrm{B(H)}},\end{aligned} \tag{5}$$

where $K_{\mathrm{DS}}=[\mathrm{S}]_{\mathrm{org}}[\mathrm{S}]^{-1}$ and $K_{\mathrm{HS}}=[\mathrm{H}^+][\mathrm{S}][\mathrm{HS}^+]^{-1}$. Here $\mathrm{p}K_{\mathrm{HS}}$ values are known,[4] and $K_{\mathrm{DS}}=0.80$ for pyridine, 1.87 for 2-methylpyridine, 3.30 for 3-methylpyridine, and 2.24 for 4-methylpyridine, respectively, which were obtained experimentally by the present authors. The above data and Eq. 5 enable us to calculate $\alpha_{\mathrm{B(H)}}$ for each pyridine base.

From the previous work,[2] the main species in the organic phase is FeR_2S_2 and that in the aqueous phase is FeR^+ in the high concentration region of TTA, where the extraction is assumed to proceed according to Eq. 6:

$$FeR^+ + HR_{org} + 2S_{org} \leftrightarrows FeR_2S_{2,org} + H^+, \qquad (6)$$

and the extraction constant is defined by

$$K_{ex} = \frac{[FeR_2S_2]_{org}[H^+]}{[FeR^+][HR]_{org}[S]_{org}{}^2}, \qquad (7)$$

when D value given by Eq. 1 equals $[FeR_2S_2]_{org} \times [FeR^+]^{-1}$, Eq. 7 is expressed by

$$\log D = \log K_{ex} + \log [HR]_{org} + 2\log [S]_{org} + pH. \qquad (8)$$

Since $[S]_{tot} = [S]_{org}\alpha_{B(H)}$, Eq. 8 is rewritten as

$$\log D\alpha_{B(H)}{}^2 = \log K_{ex} + \log [HR]_{org} + 2\log [S]_{tot} + pH. \quad (9)$$

In the case that the above assumption is valid, a plot of $\log D\alpha_{B(H)}{}^2$ against pH keeping $[HR]_{org}$ and $[S]_{tot}$ constant will give a straight line with a slope of unity. As seen in Figs. 1 and 2, plots fall on a straight line having a slope of unity, indicating that Eq. 9 is valid. The resulting $\log K_{ex}$ values are given in Table 1, where $\log K_{ex}$ values for pyridine and 4-methylpyridine obtained at a light place differ from those at a shaded place. In order to clarify the reason for the light and shade effect, the stability constant for a synergistic adduct was measured as is described below. By assuming that the main species extracted with TTA and pyridine base is FeR_2S_n (n=0, 1, 2), the adduct formation reaction can

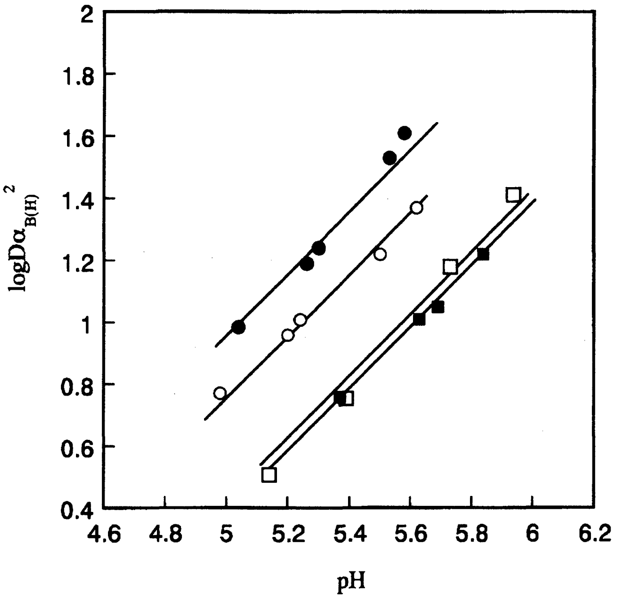

Fig. 1. Plot of $\log D\alpha_{B(H)^2}$ against pH. ○, values for pyridine at a light place; ●, values for pyridine at a shade place; □, values for 2-methylpyridine at a light place; ■, values for 2-methylpyridine at a shade place.

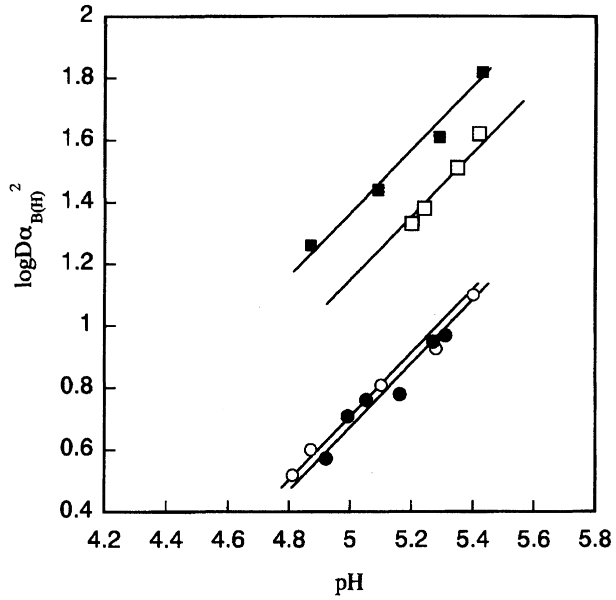

Fig. 2. Plot of $\log D\alpha_{B(H)^2}$ against pH. ○, values for 3-methylpyridine at a light place; ●, values for 3-methylpyridine at a shade place; □, values for 4-methylpyridine at a light place; ■, values for 4-methylpyridine at a shade place.

Table 1. Summary of $\log K_{ex}$ Values

Additive	$\log K_{ex}$	
	Light place	Shade place
Pyridine	4.47	4.97
2-Methylpyridine	4.42	4.38
3-Methylpyridine	4.70	4.68
4-Methylpyridine	5.18	5.37

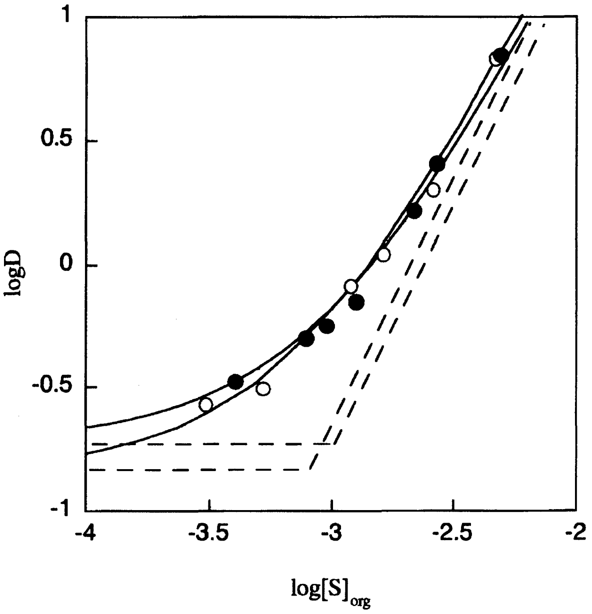

Fig. 3. Plot of $\log D$ against $\log [S]_{org}$. ○, values for pyridine at a light place; ●, values for pyridine at a shade place; —, normalized curve defined in Eq. 14; ---, asymptote.

Table 2. Summary of Constants

Additive		$\log D_0$	$\log \beta_1$	$\log \beta_2$
Pyridine	Light place	−0.82	2.88	5.40
	Shade place	−0.70	2.84	5.32
4-Methylpyridine	Light place	−0.85	3.07	6.13
	Shade place	−0.68	3.19	6.02

be expressed by

$$\mathrm{FeR}_{2,\mathrm{org}} + n\mathrm{S}_{\mathrm{org}} \leftrightarrows \mathrm{FeR_2S}_{n,\mathrm{org}}, \tag{10}$$

for which the stability constant is defined as

$$\beta_n = \frac{[\mathrm{FeR_2S}_n]_{\mathrm{org}}}{[\mathrm{FeR_2}]_{\mathrm{org}}[\mathrm{S}]_{\mathrm{org}}{}^n}. \tag{11}$$

Then, the distribution ratio given by Eq. 2 can be written as

$$\begin{aligned} D &= \frac{[\mathrm{FeR_2}]_{\mathrm{org}} + [\mathrm{FeR_2S}]_{\mathrm{org}} + [\mathrm{FeR_2S_2}]_{\mathrm{org}}}{[\mathrm{Fe^{II}}]} \\ &= D_0(1 + \beta_1[\mathrm{S}]_{\mathrm{org}} + \beta_2[\mathrm{S}]_{\mathrm{org}}{}^2), \end{aligned} \tag{12}$$

where $D_0 = [\mathrm{FeR_2}]_{\mathrm{org}}[\mathrm{Fe^{II}}]^{-1}$. Taking logarithms, Eq. 12 gives

$$\log D - \log D_0 = \log(1 + \beta_1[\mathrm{S}]_{\mathrm{org}} + \beta_2[\mathrm{S}]_{\mathrm{org}}{}^2). \tag{13}$$

Equation 13 can be expressed by a normalized curve (Eq. 14), by taking $v^2 = \beta_2[\mathrm{S}]_{\mathrm{org}}{}^2$, $p = \beta_1\beta_2^{-1/2}$ and $Y = \log D - \log D_0$;

$$Y = \log(1 + pv + v^2). \tag{14}$$

As a result of curve-fitting, in which our data well fits Eq. 14 (Figs. 3 and 4), the results are summarized in Table 2, where no light and shade effect is seen in $\log \beta_1$ and $\log \beta_2$ values. On the contrary, the $\log D_0$ value exhibits the light and shade effect, indicating that the above effect occurs in bonds between the central $\mathrm{Fe^{2+}}$ and TTA anions.

Back-coordination from metal to pyridine antibonding π-orbitals should localize charge principally on the 2-, 4-, and 6-positions. Thus any substituent, such as 3-alkyl, which directs charge to these same positions will have the effect of inhibiting metal-ligand π-bonding. 4-Alkyl substituents direct charge mainly out of the 1-, 3-, and 5-positions, and back bonding is therefore not inhibited to the same degree.[5] The π back-donation in the 3-methylpyridine system can not be expected and the same situation exists in the 2-methylpyridine system, because of the steric hindrance caused by the presence of 2-methyl group. These are reasons for there being no light and shade effect on the extraction of iron(II) with TTA and 2-methyl or 3-methylpyridine. On the other hand, in the case of the pyridine and 4-methylpyridine system, the π back-donation reduces the density of d_π electrons on iron(II) ion, which causes the formation of an increased p_π–d_π bonding with oxygen atom of TTA anion. The π electrons may transfer to the excited state at a light place, where the iron(II)-TTA bonding is expected to be weakened. In fact, smaller values of $\log K_{\mathrm{ex}}$ and $\log D_0$ are obtained at a light place compared with those obtained at a shaded place.

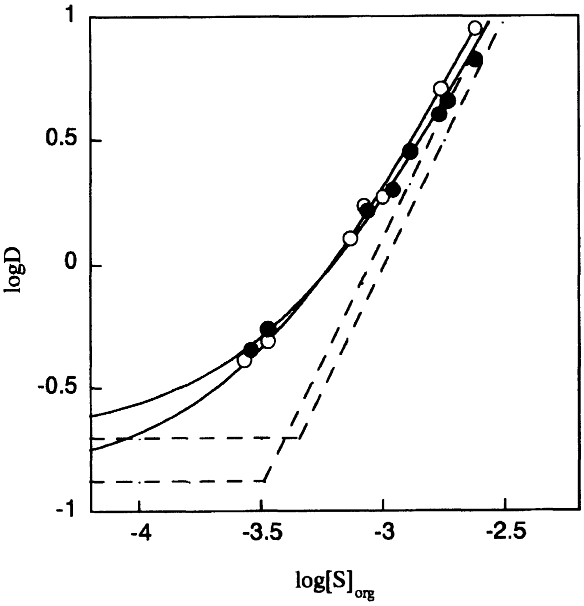

Fig. 4. Plot of $\log D$ against $\log [\mathrm{S}]_{\mathrm{org}}$. ○, values for 4-methylpyridine at a light place; ●, values for 4-methylpyridine at a shade place; —, normalized curve defined in Eq. 14; - - -, asymptote.

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