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Oxidation of Iron(II) during Solvent Extraction with Benzoyltrifluoroacetone into Carbon Tetrachloride in the Absence and Presence of Tetrabutylammonium Ion or Trioctylphosphine Oxide

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The solvent extraction of iron(II) in aqueous 0.1 mol dm^{-3} sodium nitrate solutions containing ascorbic acid with benzoyltrifluoroacetone (Hbfa) into carbon tetrachloride was studied in the absence and presence of tetrabutylammonium ion (tba$^+$) or trioctylphosphine oxide (TOPO). By the addition of tba$^+$, the tba$^+$Fe(bfa)$_3^-$ species, and by the addition of TOPO, the Fe(bfa)$_2$TOPO$_n$ (n=1 or 2) species were extracted in addition to the Fe(bfa)$_2$ species and the extraction was greatly enhanced. The iron(II) in the benzoyltrifluoroacetonate complex extracted in the organic phase was oxidized rather quickly and the rate of this oxidation was also studied. An addition of tba$^+$ or TOPO to the system slowed down the oxidation reaction, and the reason for the effects of tba$^+$ and TOPO on the rate of oxidation is discussed.

Much less has been studied of the chelate extraction of iron(II) than that of iron(III), maybe because iron(II) is often oxidized to iron(III) during solvent extraction and the results are not reproducible. For this reason, the kinetic study of oxidation of iron(II) during its solvent extraction should be indispensable for the reasonable and systematic understanding of the solvent extraction behavior of iron(II).

Such oxidations of metal ions during solvent extraction were reported by us.[1)] It was found that cerium(III) was oxidized to cerium(IV) in the organic phase during its solvent extraction with 1-phenyl-4,4,4-trifluorobutane-1,3-dione (benzoyltrifluoroacetone, Hbfa). It was also found that the extraction of cerium(III) with Hbfa was very much enhanced by an addition of tetrabutylammonium ion (tba$^+$) due to the extraction of the anionic complex as ion-pairs with tba$^+$, tba$^+$Ce(bfa)$_4^-$ in addition to the neutral complex, Ce(bfa)$_3$. Furthermore, it was found that the oxidation of the extracted cerium(III) in the tba$^+$Ce(bfa)$_4^-$ species was negligible.

In this paper, the solvent extraction of iron(II) from aqueous solutions that contained an effective reductant for iron(III), ascorbic acid, into carbon tetrachloride with Hbfa was studied. The effects of tba$^+$ or trioctylphosphine oxide (TOPO) on the extraction equilibrium and on the rate of oxidation of iron(II) in the complex in the organic phase were also studied. We discuss the enhancement of extraction and the change in the rate of oxidation caused by tba$^+$ or TOPO.

Experimental

The experiments were done at 298 K in an essentially similar manner as in our previous studies.[1,2)] Stoppered glass tubes (capacity 20 cm^3) were used for the solvent extraction experiments. The aqueous phase was a 0.1 mol dm^{-3} sodium nitrate solution and was buffered between pH 3.2 and 5.5 by acetate. The initial concentration of iron(II) for the equilibrium study was 2×10^{-5} mol dm^{-3} and that for the kinetic study was 1×10^{-4} mol dm^{-3}. The aqueous phase had added 1×10^{-2} mol dm^{-3} ascorbic acid to prevent the oxidation of iron(II). The volume of the two phases was always 5 cm^3. They were agitated vigorously by a mechanical shaker for 30 s and centrifuged. The hydrogen-ion concentration in the aqueous phase was measured by potentiometry. The extracted metal ion in the organic phase was stripped by 4 mol dm^{-3} nitric acid. The iron in the aqueous solution was measured by an atomic absorption method.

The iron(III) produced by the oxidation of iron(II) in the benzoyltrifluoroacetonate complex in carbon tetrachloride was measured by spectrophotometry: The absorbance of this organic solution at 380 nm was recorded every 30 s, usually for 15 min. However, when tba$^+$ or TOPO was added and thus, the rate of oxidation was slowed down, the measurements were continued for a longer period. Some experiments were also done by equilibrating the system with 1 atm oxygen gas but otherwise in the same way as above.

Statistical

The statistical analysis of the data was done in a similar manner as described in our previous papers.[1,2)] Thus only representative equations are given here:

$$[\text{Hbfa}]_{\text{org,init}} = [\text{Hbfa}]_{\text{org}} + [\text{Hbfa}] + [\text{bfa}^-] \tag{1}$$

$$[\text{bfa}^-] = [\text{Hbfa}]_{\text{org,init}}/\{1 + (1 + K_\text{d})K_\text{a}{}^{-1}[\text{H}^+]\} \tag{2}$$

where $K_\text{a} = [\text{H}^+][\text{bfa}^-][\text{Hbfa}]^{-1}$ and $K_\text{d} = [\text{Hbfa}]_{\text{org}} \times[\text{Hbfa}]^{-1}$. The distribution ratio can be written as follows:

$$\begin{aligned} D_0 &= [\text{Fe(bfa)}_2]_{\text{org}}/([\text{Fe}^{2+}] + [\text{Fe(bfa)}^+]\cdots) \\ &= K_{\text{ex}2,0}[\text{bfa}^-]^2/(1 + \textstyle\sum\beta_n[\text{bfa}^-]^n) \end{aligned} \tag{3}$$

$$K_{\text{ex}2,0} = [\text{Fe(bfa)}_2]_{\text{org}}[\text{Fe}^{2+}]^{-1}[\text{bfa}^-]^{-2} \tag{4}$$

$$\beta_n = [\text{Fe(bfa)}_n{}^{2-n}][\text{Fe}^{2+}]^{-1}[\text{bfa}^-]^{-n} \tag{5}$$

In the presence of bulky cations (tba$^+$), the distribution ratio can be written as:

$$\begin{aligned} D = ([\text{Fe(bfa)}_2]_{\text{org}} + [\text{tba}^+\text{Fe(bfa)}_3{}^-]_{\text{org}}) \\ /([\text{Fe}^{2+}] + [\text{Fe(bfa)}^+] + \cdots) \end{aligned}$$

$$= (K_{\mathrm{ex2,0}}[\mathrm{bfa}^-]^2 + K_{\mathrm{ex3,1}}[\mathrm{bfa}^-]^3[\mathrm{tba}^+]) /(1 + \sum\beta_n[\mathrm{bfa}^-]^n) \quad (6)$$

$$D[\mathrm{bfa}^-]^{-2} = (K_{\mathrm{ex2,0}} + K_{\mathrm{ex3,1}}[\mathrm{bfa}^-][\mathrm{tba}^+])/(1+\sum\beta_n[\mathrm{bfa}^-]^n) \quad (7)$$

and

$$K_{\mathrm{ex3,1}} = [\mathrm{tba}^+\mathrm{Fe(bfa)_3}^-]_{\mathrm{org}}[\mathrm{Fe}^{2+}]^{-1}[\mathrm{bfa}^-]^{-3}[\mathrm{tba}^+]^{-1} \quad (8)$$

The following equation can be introduced:

$$D^*/D_0{}^* = 1 + (K_{\mathrm{ex3,1}}/K_{\mathrm{ex2,0}})[\mathrm{bfa}^-][\mathrm{tba}^+] \quad (9)$$

where $D_0{}^*$ is $D_0 \times [\mathrm{bfa}^-]^{-2}$ and D^* is $D \times [\mathrm{bfa}^-]^{-2}$. The extraction of anionic complex as ion-pairs with the cation can also be given as:

$$K_{\mathrm{org}} = [\mathrm{tba}^+\mathrm{Fe(bfa)_3}^-]_{\mathrm{org}}[\mathrm{Fe(bfa)_2}]_{\mathrm{org}}{}^{-1}[\mathrm{tba}^+\mathrm{bfa}^-]_{\mathrm{org}}{}^{-1} \quad (10)$$

$$K_{\mathrm{exAB}} = [\mathrm{tba}^+\mathrm{bfa}^-]_{\mathrm{org}}[\mathrm{bfa}^-]^{-1}[\mathrm{tba}^+]^{-1} \quad (11)$$

and from Eqs. 4, 7, 8, 9, and 11 the following equations can be written:

$$K_{\mathrm{org}} = K_{\mathrm{ex3,1}}K_{\mathrm{ex2,0}}{}^{-1}K_{\mathrm{exAB}}{}^{-1} \quad (12)$$

$$D = K_{\mathrm{ex2,0}}[\mathrm{bfa}^-]^2(1 + K_{\mathrm{org}}K_{\mathrm{exAB}}[\mathrm{bfa}^-][\mathrm{tba}^+])/(1 + \sum\beta_n[\mathrm{bfa}^-]^n)$$

The enhancement of extraction can be written more clearly as:

$$D^*/D_0{}^* = 1 + K_{\mathrm{org}}K_{\mathrm{exAB}}[\mathrm{bfa}^-][\mathrm{tba}^+] \quad (13)$$

When the non-charged chelate forms adducts with n molecules of a neutral ligand (L) such as TOPO in the organic phase, the distribution ratio in the presence of L can generally be written:

$$D = ([\mathrm{Fe(bfa)_2}]_{\mathrm{org}} + [\mathrm{Fe(bfa)_2L}]_{\mathrm{org}} + [\mathrm{Fe(bfa)_2L_2}]_{\mathrm{org}} + \cdots) /([\mathrm{Fe}^{2+}] + [\mathrm{Fe(bfa)}^+] + \cdots)$$
$$= K_{\mathrm{ex2,0}}[\mathrm{bfa}^-]^2(1 + \beta_{(\mathrm{org})1}[\mathrm{L}]_{\mathrm{org}} + \beta_{(\mathrm{org})2}[\mathrm{L}]_{\mathrm{org}}{}^2 + \cdots) /(1 + \sum\beta_n[\mathrm{bfa}^-]^n) \quad (14)$$

where

$$\beta_{(\mathrm{org})n} = [\mathrm{Fe(bfa)_2L}_n]_{\mathrm{org}}[\mathrm{Fe(bfa)_2}]_{\mathrm{org}}{}^{-1}[\mathrm{L}]_{\mathrm{org}}{}^{-n} \quad (15)$$

The following equation can be introduced from Eqs. 3 and 14 where $D_0{}^*$ and D^* are the same as already given:

$$D^*/D_0{}^* = 1 + \beta_{(\mathrm{org})1}[\mathrm{L}]_{\mathrm{org}} + \beta_{(\mathrm{org})2}[\mathrm{L}]_{\mathrm{org}}{}^2 + \cdots \quad (16)$$

For these calculations, the concentration of tba^+ at equilibrium should be used; it can be obtained by

$$[\mathrm{tba}^+]_{\mathrm{init}} = [\mathrm{tba}^+] + [\mathrm{tba}^+\mathrm{Fe(bfa)_3}^-]_{\mathrm{org}} + [\mathrm{tba}^+\mathrm{bfa}^-]_{\mathrm{org}} + [\mathrm{tba}^+\mathrm{NO_3}^-]_{\mathrm{org}} \quad (17)$$

$$K_{\mathrm{exXB}} = [\mathrm{tba}^+\mathrm{NO_3}^-]_{\mathrm{org}}[\mathrm{tba}^+]^{-1}[\mathrm{NO_3}^-]^{-1} \quad (18)$$

However, since the extraction of the $\mathrm{tba}^+\mathrm{NO_3}^-$ ion-pairs is negligible when the solvent is carbon tetrachloride,[3] this term will not be considered in this paper.

The concentration of TOPO at equilibrium should be given as:

$$[\mathrm{TOPO}]_{\mathrm{org,init}} = [\mathrm{TOPO}]_{\mathrm{org}} + [\mathrm{TOPO}] + [\mathrm{Fe(bfa)_2TOPO}]_{\mathrm{org}} + 2[\mathrm{Fe(bfa)_2(TOPO)_2}]_{\mathrm{org}} + \cdots + [\mathrm{Hbfa{\cdot}TOPO}]_{\mathrm{org}} \quad (19)$$

The concentration of the associated TOPO with Hbfa can be calculated by using the following equation:

$$K_{\mathrm{ass}} = [\mathrm{Hbfa{\cdot}TOPO}]_{\mathrm{org}}[\mathrm{Hbfa}]_{\mathrm{org}}{}^{-1}[\mathrm{TOPO}]_{\mathrm{org}}{}^{-1} \quad (20)$$

When iron(II) in the benzoyltrifluoroacetonate complex in the organic phase is oxidized to iron(III), as long as the backward reaction is negligible, the rate can be written as:

$$v = -\mathrm{d}[\mathrm{Fe(II)}]_{\mathrm{org}}/\mathrm{d}t = k[\mathrm{Fe(II)}]_{\mathrm{org}}[\mathrm{Hbfa}]_{\mathrm{org}}{}^a[\mathrm{O_2}]_{\mathrm{org}}{}^b\cdots \quad (21)$$

where k is the rate constant and a, b, $\cdots$ are the dependence of the rate on each component in the system. From this, the following equations are obtained:

$$-\mathrm{d}[\mathrm{Fe(II)}]_{\mathrm{org}}/[\mathrm{Fe(II)}]_{\mathrm{org}} = k[\mathrm{Hbfa}]_{\mathrm{org}}{}^a[\mathrm{O_2}]_{\mathrm{org}}{}^b\cdots\mathrm{d}t \quad (22)$$

$$-\log([\mathrm{Fe(II)}]_{\mathrm{org}}/[\mathrm{Fe(II)}]_{\mathrm{org,init}}) = k_{\mathrm{obsd\ 0}} \times t/2.303 \quad (23)$$

Here, $k_{\mathrm{obsd\,0}}$ is the observed rate constant, which can be written:

$$k_{\mathrm{obsd\ 0}} = k[\mathrm{Hbfa}]_{\mathrm{org}}{}^a[\mathrm{O_2}]_{\mathrm{org}}{}^b\cdots \quad (24)$$

When TOPO is added, the oxidation of iron(II) in the three species, $\mathrm{Fe(bfa)_2}$, $\mathrm{Fe(bfa)_2TOPO}$, and $\mathrm{Fe(bfa)_2(TOPO)_2}$ may occur. Thus the rate is described as follows:

$$v = -\mathrm{d}[\mathrm{Fe(II)}]_{\mathrm{org,total}}/\mathrm{d}t = k_{\mathrm{obsd\ 0}}[\mathrm{Fe(bfa)_2}]_{\mathrm{org}} + k_{\mathrm{obsd\ TOPO1}}[\mathrm{Fe(bfa)_2TOPO}]_{\mathrm{org}} + k_{\mathrm{obsd\ TOPO2}}[\mathrm{Fe(bfa)_2(TOPO)_2}]_{\mathrm{org}} \quad (25)$$

where

$$[\mathrm{Fe(II)}]_{\mathrm{org,total}} = [\mathrm{Fe(bfa)_2}]_{\mathrm{org}} + [\mathrm{Fe(bfa)_2TOPO}]_{\mathrm{org}} + [\mathrm{Fe(bfa)_2(TOPO)_2}]_{\mathrm{org}} \quad (26)$$

By introducing the formation constants given by Eq. 15 and by using the relation given Eq. 14, when the following R term is defined;

$$R = 1/(1 + \beta_{(\mathrm{org})1}[\mathrm{TOPO}]_{\mathrm{org}} + \beta_{(\mathrm{org})2}[\mathrm{TOPO}]_{\mathrm{org}}{}^2) \quad (27)$$

Equation 25 can be rewritten as follows:

$$-\mathrm{d}[\mathrm{Fe(II)}]_{\mathrm{org,total}}/\mathrm{d}t$$
$$= [\mathrm{Fe(bfa)_2}]_{\mathrm{org,total}}(k_{\mathrm{obsd}\ 0}R + k_{\mathrm{obsd\ TOPO1}}R\beta_{\mathrm{(org)1}}[\mathrm{TOPO}]_{\mathrm{org}} + k_{\mathrm{obsd\ TOPO2}}R\beta_{\mathrm{(org)2}}[\mathrm{TOPO}]_{\mathrm{org}}{}^2) \qquad (28)$$

The quantity in the parenthesis in Eq. 28 should be a constant at a certain given $[\mathrm{TOPO}]_{\mathrm{org}}$ (it will be written as C) and it will be abbreviated by $k_{\mathrm{obsd\ TOPO}}$;

$$k_{\mathrm{obsd\ TOPO}} = R(k_{\mathrm{obsd}\ 0} + k_{\mathrm{obsd\ TOPO1}}\beta_{\mathrm{(org)1}}C + k_{\mathrm{obsd\ TOPO2}}\beta_{\mathrm{(org)2}}C^2) \qquad (29)$$

Similar equations can be written for the rate of oxidation in the presence of tba^+. However, since the oxidation was negligible in the presence of tba^+ under the conditions of this study, these equations are not given here.

Results

When the aqueous phase containing iron(II), the buffer, and ascorbic acid was agitated with the organic phase containing Hbfa, a rapid extraction of the metal ion occured and a transient extraction equilibrium was established by a two-phase agitation for 30 s. However, when the agitation was continued for a longer period, the distribution ratio increased gradually and the organic phase changed from colorless to brownish. From these, it was estimated that the extraction equilibrium of iron(II) was established and it could be measured by the two-phase agitation for 30 s. It was pointed out that a tautomeric change of the enol form to the keto form of a certain β-diketone affected the solvent extraction of the metal ion when the two-phase agitation was continued only for 30 s. However, it was also reported that this type of effect was negligible when benzoyltrifluoroacetone was used.[4] Thus these results can be used for the consideration of the iron(II) extraction equilibrium with this β-diketone. However, the distribution ratio increased gradually until it reached a certain value after the two-phase agitation for a long time. Figure 1 gives the results.

The increase in the distribution ratio is due to the extraction of iron(III) with Hbfa being much better than iron(II). For this reason, most of the $\mathrm{Fe(bfa)_3}$ produced by oxidation of iron(II) remains in the organic phase and the decrease of iron(II) is compensated for by the extraction from the aqueous phase. Thus the transient extraction equilibrium of iron(II) should always be maintained. When iron(II) extracted as the $\mathrm{Fe(bfa)_2}$ is oxidized in the organic phase, the back-extraction of $\mathrm{Fe(bfa)_3}$ is not easy because of the high distribution constant,[5] $K_{\mathrm{dim}} = [\mathrm{Fe(bfa)_3}]_{\mathrm{org}}[\mathrm{Fe(bfa)_3}]^{-1}$, and also of the kinetically inert nature of iron(III); the dissociation of bfa^- and the reduction of iron(III) in the iron(III) complex should be rather slow.[6] This type of increase of the extraction of metal ions by oxidation, which produces a more extractable higher oxidation state has been found in other extraction systems.[7,8]

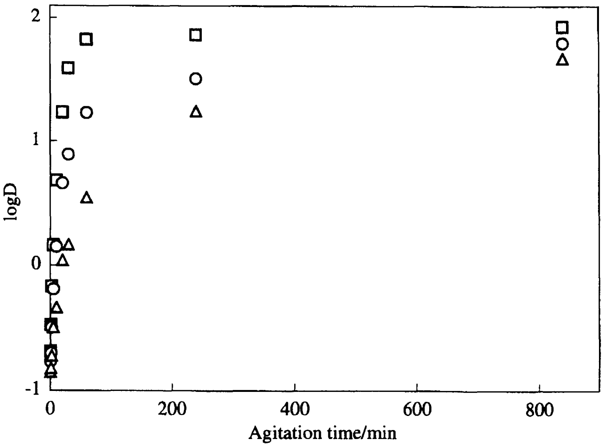

Fig. 1. Distribution ratio of iron as a function of two-phase agitation time. Aq. phase: 0.1 mol dm^{-3} $\mathrm{NaNO_3}$ containing 0.01 mol dm^{-3} ascorbic acid, acetate buffer; the initial concentration of iron(II) is 2×10^{-5} mol dm^{-3}. The $-\log[\mathrm{H}^+]$ is 3.8 (△), 4.0 (○), and 4.2 (□). org. phase: $\mathrm{CCl_4}$ containing 0.1 mol dm^{-3} Hbfa at initial.

Figure 2 gives the distribution ratio as a function of the bfa^- concentration in the aqueous phase when the two phases were agitated for 30 s. The squares show the data in the absence of tba^+ and TOPO. Figure 2 also gives the extraction data when 1×10^{-3} mol dm^{-3} of tba^+ (initial) or when 1×10^{-3} mol dm^{-3} of TOPO (initial) was added. The extraction was greatly enhanced by the addition of either tba^+ or TOPO.

Figure 3 gives the enhancement of extraction as a function of the quantity $([\mathrm{tba}^+][\mathrm{bfa}^-])$ as given in Eq. 7.

Figure 4 gives the enhancement of extraction as a function of the concentration of TOPO added to the organic phase (synergistic effect).

The data in Figs. 2, 3, and 4 were analysed by using a least-squares computer program on the basis of the equations in the statistical part (Eqs. 3, 6, 7, 14, 16, 17, and 19). The values of the constants employed in these calculations are given in the lower part of Table 1. The equilibrium constants obtained are listed in Table 1. The solid lines for each set of extraction data were calculated on the basis of the equations into which were introduced the values of constants in Table 1. Since the plots fit well with the experimental data, the values should be reasonable.

As seen from Fig. 1, the distribution ratio was enhanced by the prolonged two-phase agitation probably due to the oxidation of iron(II) in the complex to iron(III) in the organic phase. This was further measured from the change in the optical absorption of the organic phase from which the iron(II) was extracted with Hbfa; then it was separated from the aqueous phase.

From the absorbance of $\mathrm{Fe(bfa)_3}$ in carbon tetrachloride at 380 nm, where the absorption due to the $\mathrm{Fe(bfa)_2}$

Table 1. Summary of Equilibrium Constants

Solvent	$\log K_{\mathrm{ex2,0}}$	$\log \beta_1$	$\log \beta_2$	$\log K_{\mathrm{ex3,1}}$	$\log K_{\mathrm{org}}$	$\log \beta_{\mathrm{(org)1}}$	$\log \beta_{\mathrm{(org)2}}$	Remark
CCl_4	10.2	4.7	9.2	20.2	8.7	5.6	7.7	Present work
$CHCl_3$	10.0	4.2	8.0	21.6	7.6	—	—	Ref. 9

The values of equilibrium constants of benzoyltrifluoroacetone used in the calculations are as follows. K_a is $10^{-6.03}$, K_{dm} is $10^{2.39}$ (Ref. 11), K_{exAB} is $10^{1.27}$ (Ref. 10), K_{exXB} is 0 (Ref. 3) and K_{ass} in Eq. 20 is $10^{0.59}$ (Ref. 2) when the organic phase is CCl_4 and the aqueous phase is 0.1 mol dm^{-3} $NaNO_3$ or $NaClO_4$.

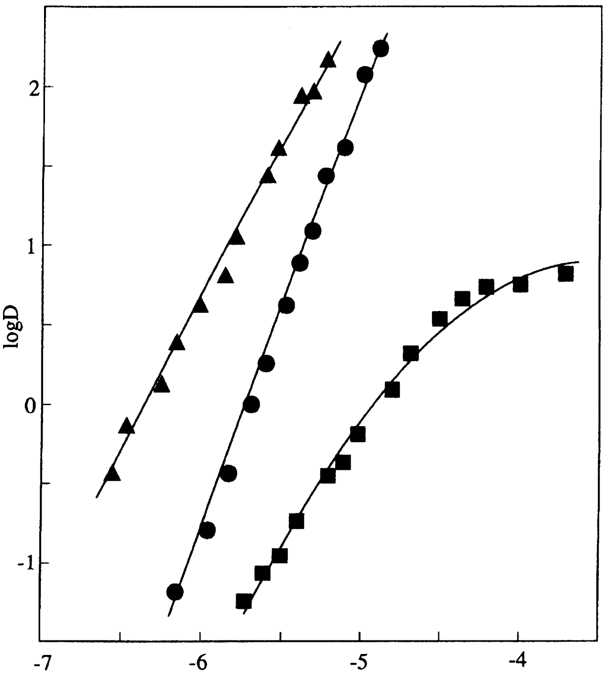

Fig. 2. Distribution ratio of iron(II) as a function of bfa$^-$ concentration when the two phases are agitated for 30 s. Aq phase: 0.1 mol dm^{-3} $NaNO_3$ containing 0.01 mol dm^{-3} ascorbic acid and acetate buffer. The initial concentration of iron(II) is 2×10^{-5} mol dm^{-3}. Org. phase: CCl_4 initially containing 0.1 mol dm^{-3} Hbfa and the system contained neither tba$^+$ nor TOPO (■); the aqueous phase of the system is initially containing 1.0×10^{-3} mol dm^{-3} tba$^+$ (●); the organic phase of the system is initially containing 1.0×10^{-3} mol dm^{-3} TOPO (▲). The line for each plot is calculated on the basis of Eqs. 3, 6, and 14, each of which is introduced the values of constants in Table 1, respectively.

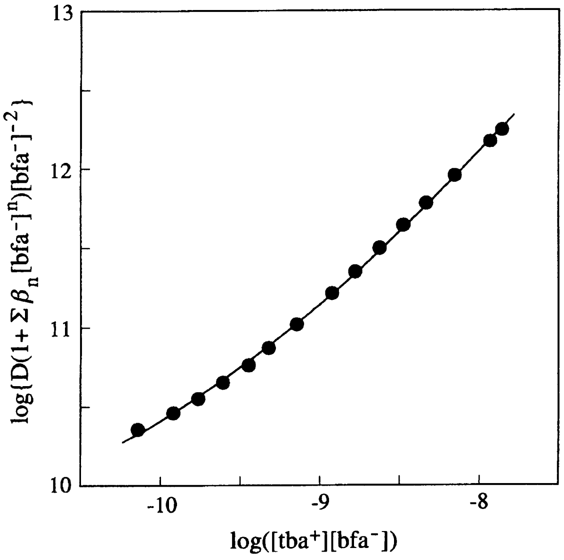

Fig. 3. Enhancement of extraction of iron(II) given as a function of the [tba$^+$][bfa$^-$] value at equilibrium when the two phases are agitated for 30 s. Org. phase: CCl_4 containing 0.1 mol dm^{-3} Hbfa at initial. Aq phase: 0.1 mol dm^{-3} $NaNO_3$ containing 0.01 mol dm^{-3} ascorbic acid, 2×10^{-5} mol dm^{-3} iron(II) at initial, and tba$^+$ at various concentrations. The $-\log[H^+]$ is in the range from 3.79 to 3.83. The line is calculated on the basis of Eqs. 7 and 17.

was negligible, the molar extinction coefficient of the $Fe(bfa)_3$ was obtained to be 8.5×10^3 mol dm^{-3} cm^{-1}. From this, the amount of Fe(III) produced was calculated and from the data, the $-\log([\mathrm{Fe(II)}]_{\mathrm{org}}/[\mathrm{Fe(II)}]_{\mathrm{org,init}})$ vs. time plot was made. The value of $k_{\mathrm{obsd\,0}}$ was calculated from the slope of plot on the basis of Eq. 23. Figure 5 gives the $\log k_{\mathrm{obsd\,0}}$ vs. $\log[\mathrm{Hbfa}]_{\mathrm{org}}$ plot. As seen from Fig. 5, the value of $\log k_{\mathrm{obsd\,0}}$ was not affected by the Hbfa concentration. The $\log k_{\mathrm{obsd\,0}}/\mathrm{s}^{-1}$ was obtained from these data to be -2.50.

Figure 6 gives the effect of TOPO on the rate of oxidation in the organic phase that had been separated from the aqueous phase. From the slope of the plots in Fig. 6, the $k_{\mathrm{obsd\,TOPO}}$ in Eq. 29 at each TOPO concentration was obtained. The $\log k_{\mathrm{obsd\,TOPO}}$ vs. $\log[\mathrm{TOPO}]_{\mathrm{org}}$ plot obtained from the data in Fig. 6 is given in Fig. 7a. As in seen from Fig. 7a, the rate is inverse first order with respect to the TOPO concentration when it is higher than 0.03 mol dm^{-3}. From Fig. 7a it can be assumed that $k_{\mathrm{obsd\,TOPO2}}$ in Eq. 25 should be much smaller than $k_{\mathrm{obsd\,TOPO1}}$. If $k_{\mathrm{obsd\,TOPO2}}$ is negligiblly small, then Eq. 29 can be written as;

$$k_{\mathrm{obsd\,TOPO}} = R(k_{\mathrm{obsd\,0}} + k_{\mathrm{obsd\,TOPO1}}\beta_{\mathrm{(org)1}}[\mathrm{TOPO}]_{\mathrm{org}}) \tag{30}$$

In the lowest $[\mathrm{TOPO}]_{\mathrm{org}}$ region in Fig. 7a, the $Fe(bfa)_2$ species should be negligible as could be assumed from Fig. 7b. Although the calculation for Fig. 7b was made on the basis of equilibrium data, this could be at least approximately accepted. Thus Eq. 30 would be represented by

$$k_{\mathrm{obsd\,TOPO}} = k_{\mathrm{obsd\,TOPO1}} \tag{31}$$

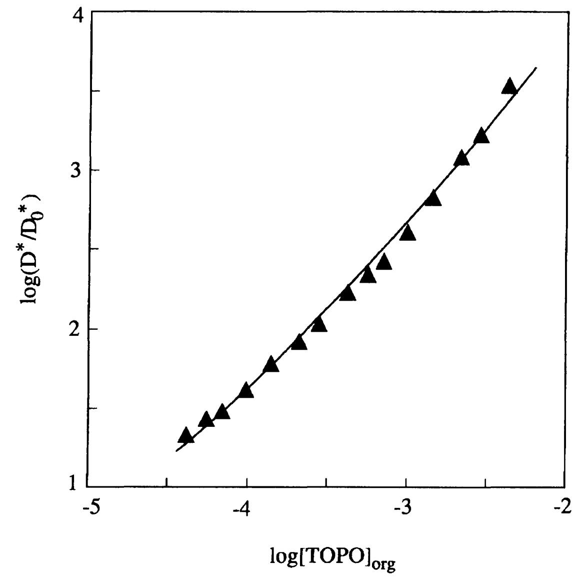

Fig. 4. Enhancement of extraction of iron(II) as a function of TOPO concentration at equilibrium when the two phases are agitated for 30 s. Org. phase: CCl_4 containing Hbfa 0.1 mol dm^{-3} and TOPO at various concentration. Aq phase: 0.1 mol dm^{-3} $NaNO_3$ containing 0.01 mol dm^{-3} ascorbic acid and 2×10^{-5} mol dm^{-3} iron(II) at initial. The $-\log[H^+]$ is in the range from 3.27 to 3.29. About D^* and $D_0{}^*$, see the text. The line is calculated on the basis of Eqs. 16 and 19.

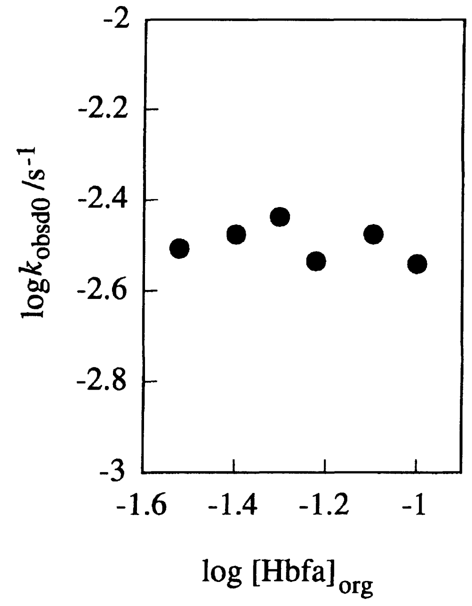

Fig. 5. Dependence of the rate of oxidation of iron(II) in the Fe(bfa)$_2$ complex in CCl_4 on the Hbfa concentration. (cf. Eq. 24).

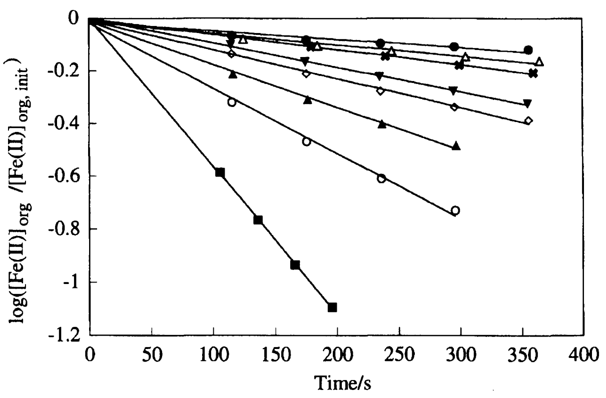

Fig. 6. Rate of oxidation of iron(II) in the Fe(bfa)$_2$ complex in CCl_4 containing Hbfa at 0.05 mol dm^{-3} and TOPO at various concentration. The TOPO concentration is 6×10^{-2}, 4×10^{-2}, 2×10^{-2}, 1×10^{-2}, 8×10^{-3}, 6×10^{-3}, 4×10^{-3}, and 0 mol dm^{-3} from the top to the bottom. (cf. Eqs. 23 and 25).

In the highest $[\mathrm{TOPO}]_{\mathrm{org}}$ region, on the other hand, it would be represented by

$$k_{\mathrm{obsd\ TOPO}} = k_{\mathrm{obsd\ TOPO1}}\beta_{(\mathrm{org})1}\beta_{(\mathrm{org})2}{}^{-1}[\mathrm{TOPO}]_{\mathrm{org}}{}^{-1} \tag{32}$$

Equations 31 and 32 should give the two asymptotes in Fig. 7a and from these asymptotes, it is estimated that $k_{\mathrm{obsd\,TOPO1}}$ is $10^{-2.5}$ (s^{-1}) and the value of the term $k_{\mathrm{obsd\,TOPO1}}\ \beta_{(\mathrm{org})1}\ \beta_{(\mathrm{org})2}{}^{-1}$ is $10^{-4.9}$ (s^{-1}). Furthermore, $k_{\mathrm{obsd\,TOPO1}}$ seems to be quite similar to $k_{\mathrm{obsd\,0}}$ because the most part of Fe(II) in the organic solution at the lower concentration range of TOPO in Fig. 7a is in the form of Fe(bfa)$_2$TOPO and the rate of oxidation is quite similar to that obtained in the absence of TOPO.

The effects of oxygen concentration in the organic solvent were also studied. The rate of oxidation was measured when the organic solvent contained 0.05 mol dm^{-3} Hbfa and 0.01 to 0.1 mol dm^{-3} TOPO and was saturated with 1 atm oxygen gas. The rate of oxidation was found to be similar to that when the solvent was saturated with 1 atm air within the experimental accuracy.

When the aqueous phase had tba$^+$ added and thus, the tba$^+$Fe(bfa)$_3{}^-$ complex was extracted in addition to the Fe(bfa)$_2$ species, the rate of oxidation of iron(II) in the organic phase was slowed down. This was explained by the rate of oxidation of iron(II) in the tba$^+$Fe(bfa)$_3{}^-$ complex in the organic phase being extremely low.

The addition of a small amount of tba$^+$ interfered with the oxidation very much. When $[\mathrm{tba}^+]_{\mathrm{init}}$ was higher than 1×10^{-2} mol dm^{-3} under the conditions where [bfa$^-$] was $10^{-5.9}$, the oxidation was nearly negligible over one hour. It can be calculated on the basis of Eq. 13 that 1.3% of the total iron in the organic phase was in the form of Fe(bfa)$_2$ and the rest was in the form of tba$^+$Fe(bfa)$_3{}^-$.

Discussion

In the aqueous phase containing ascorbic acid, the iron should be originally only in the divalent state. The observation that the extraction equilibrium was reached within 30 s should suggest that it is a transient extraction equilibrium of the iron(II) as is given by Eq. 3.

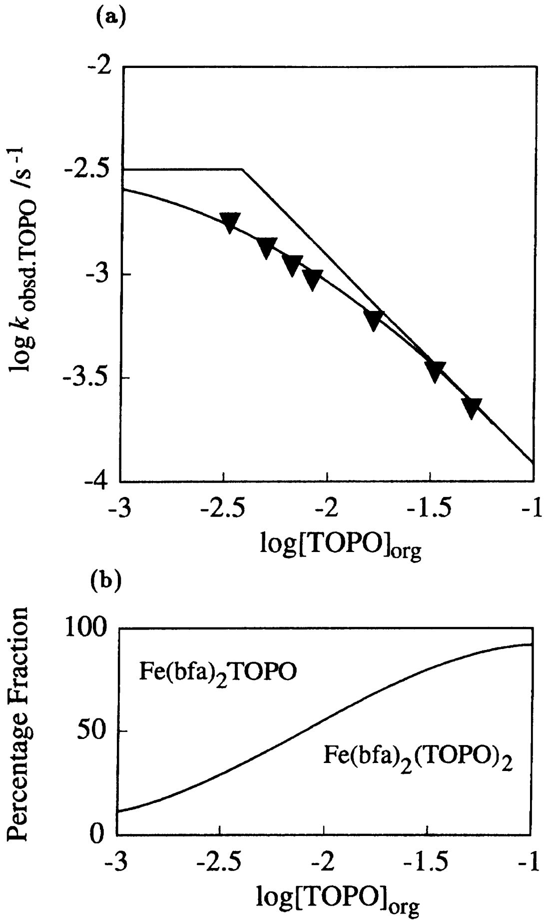

Fig. 7. (a) Effect of TOPO on the rate of oxidation of iron(II) in the Fe(bfa)$_2$ complex in CCl$_4$ given by the observed rate constant (cf. Eq. 29). (b) Percentage fraction of Fe(bfa)$_2$(TOPO) and Fe(bfa)$_2$(TOPO)$_2$ species in the equilibrated organic phase as a function of TOPO concentration calculated on the basis of Eq. 27: $\beta_{(\mathrm{org})1}$ [TOPO]$_{\mathrm{org}}$ R and $\beta_{(\mathrm{org})2}$ [TOPO]$_{\mathrm{org}}{}^2R$ using the values in Table 1.

Then the iron(II) in the complex was oxidized only in the organic phase. This is because the aqueous phase was a reducing medium but the organic phase was saturated with air. In such an oxidation reaction, the oxidant should be the atmospheric oxygen that was dissolved in the organic phase.

As is seen from Fig. 2, the slope of extraction curve of iron(II) with Hbfa is nearly +2. The deviation of the plot from a straight line of a slope of +2 is well explained by the formation of complexes with bfa$^-$ in the aqueous phase as can be seen from Eq. 3. However, as also can be seen from Fig. 2, the plot $\log D$ vs. $\log[\mathrm{bfa}^-]$ is a straight line of a slope +2 when 1×10^{-3} mol dm^{-3} of TOPO was added into the system. This is because the distribution ratio in the presence of TOPO is much higher than its absence and thus, the [bfa$^-$] that gives the same distribution ratio is much lower than that in the absence of TOPO. This decreases the effect of aqueous chelate complex that is shown by the quantity of $\sum\beta_n[\mathrm{bfa}^-]^n$ in Eq. 14 and this makes the deviation from the slope +2 negligible.

A similar type of argument is also possible for the extraction curve in the presence of tba$^+$. However, the effects of chelate formation in the aqueous phase are not negligible although they are much smaller than that in the absence of tba$^+$. The slight decrease of tba$^+$ concentration by increasing bfa$^-$ concentration as seen from Eqs. 11 and 17 should also cause a small deviation. Thus the plot calculated on the basis of Eq. 6 deviates from a straight line of a slope +3 somewhat downward.

The solvent extraction of iron(II) with Hbfa into chloroform was reported in a previous paper.[9] The equilibrium constants obtained in our previous study are also given in Table 1. The effects of the solvent are different in carbon tetrachloride and in chloroform as was found in the extraction of europium(III) with thenoyltrifluoroacetone.[10] This is also found in iron(II) complex with bfa$^-$. The extraction of the ternary complex given by Eq. 8 is better into chloroform than into carbon tetrachloride. It is seen that the association constant of the neutral complex with the ion-pair of the reagents given by K_{org} in Eq. 10 is higher in carbon tetrachloride than in chloroform. The extraction of the ion-pair of the reagents given by K_{exAB} in Eq. 11 is much higher into chloroform ($10^{4.0}$)[9] than into carbon tetrachloride and the overall effect of these makes the extraction of the ternary complex to some extent better into chloroform than into carbon tetrachloride.

When the organic phase was saturated with air, the oxidation of the extracted iron(II) in benzoyltrifluoroacetonate complex was rather rapid. The value of $k_{\mathrm{obsd}\,0}$ in carbon tetrachloride solution separated from the aqueous phase is $10^{-2.5}$ (s^{-1}) which is higher than that of cerium(III) in the complex with bfa$^-$:[1] the value is $10^{-4.4}$ (s^{-1}). After half an hour, almost all of the iron(II) in the complex in carbon tetrachloride was oxidized to iron(III).

Since the oxidation is not dependent on the Hbfa concentration in the organic solution as can be seen from Fig. 5, the rate-determining step should not be the addition of the ligand on iron(III) which is produced by the oxidation of iron(II).

The very slow oxidation of iron(II) in the ternary complex, tba$^+$Fe(bfa)$_3{}^-$, in the organic phase should be due to that the six coordination sites in the octahedral form complex of iron(II) should be occupied by the three chelating ligands and this structure should be related with the very slow oxidation.

The rate of oxidation is dependent only on the inverse first order of TOPO concentration although Fe(bfa)$_2$ could accept two TOPO molecules in the organic phase as can be seen from Fig. 4 or the value of $\beta_{(\mathrm{org})2}$ in Table 1. The inverse first order dependence of the oxidation on the TOPO concentration should be due to that the addition of the second TOPO molecule on the Fe(bfa)$_2$TOPO adduct which should be related that the six coordination sites are also occupied like as the iron(II) in the ternary complex mentioned above and thus interferes with the oxidation. From Eqs. 26 and 27, the proportion of the chemical species in the organic phase in the presence of TOPO can be calculated as given by the following equations:

$$[\mathrm{Fe(bfa)_2}]_{\mathrm{org}}/[\mathrm{Fe(II)}]_{\mathrm{org,total}} = R$$

$$[\mathrm{Fe(bfa)_2TOPO}]_{\mathrm{org}}/[\mathrm{Fe(II)}]_{\mathrm{org,total}} = \beta_{(\mathrm{org})1}[\mathrm{TOPO}]_{\mathrm{org}}R$$

$$[\mathrm{Fe(bfa)_2(TOPO)_2}]_{\mathrm{org}}/[\mathrm{Fe(II)}]_{\mathrm{org,total}} = \beta_{(\mathrm{org})2}[\mathrm{TOPO}]_{\mathrm{org}}{}^2R$$

When $[\mathrm{TOPO}]_{\mathrm{org}}=1\times10^{-3}$ mol dm^{-3}, the $[\mathrm{Fe(bfa)_2}]_{\mathrm{org}}$ is calculated to be already less than 0.2%, the $[\mathrm{Fe(bfa)_2(TOPO)_2}]_{\mathrm{org}}$ to be about 10% and the majority is in the $\mathrm{Fe(bfa)_2TOPO}$ form as is seen from Fig. 7b which gives the percentage fraction of the complex species calculated by the above equations by using the values of $\beta_{(\mathrm{org})1}$ and $\beta_{(\mathrm{org})2}$ in Table 1 from the solvent extraction equilibrium data. The rate of oxidation under these conditions is found to be nearly the same as that in the absence of TOPO. Thus the value of $k_{\mathrm{obsd\,0}}$ is nearly the same as that of $k_{\mathrm{obsd\,TOPO1}}$. It is seen from Fig. 7b that an increase in the TOPO concentration in this range changes the $\mathrm{Fe(bfa)_2TOPO}$ species to the $\mathrm{Fe(bfa)_2(TOPO)_2}$ species. This change should be the reason for the slowdown of the rate of oxidation by an increase in the TOPO concentration in this range: The decrease in the $\mathrm{Fe(bfa)_2TOPO}$ concentration (Fig. 7b) decreases the rate of oxidation (Fig. 7a). However, the effects of TOPO on the rate of oxidation by the formation of the $\mathrm{Fe(bfa)_2(TOPO)_2}$ species appear at a lower concentration than on the enhancement of the extraction by the formation of the same species. On the basis of Eq. 15, it is estimated that 50% of the $\mathrm{Fe(bfa)_2TOPO}$ changes into the $\mathrm{Fe(bfa)_2(TOPO)_2}$ species when the TOPO concentration is $10^{-2.1}$ mol dm^{-3} (cf. Fig. 7b) according to the value in Table 1 from the equilibrium data. If the oxidation of the $\mathrm{Fe(bfa)_2(TOPO)_2}$ species would be negligible compared to that of the $\mathrm{Fe(bfa)_2TOPO}$ species, the value of the $k_{\mathrm{obsd\,TOPO}}$ should become half when the half of the $\mathrm{Fe(bfa)_2TOPO}$ species changes to the $\mathrm{Fe(bfa)_2(TOPO)_2}$ form. However, as is seen from Fig. 7a, this 0.3 unit decrease of $\log k_{\mathrm{obsd\,TOPO}}$ is found when the TOPO concentration is $10^{-2.4}$, that is, the effects of the TOPO appear at a little lower TOPO concentration than that for the enhancement of the solvent extraction. In other words, the effects of TOPO are somewhat different for the solvent extraction equilibrium and for the rate of oxidation. Such a disagreement of the effects of TOPO on the rate of oxidation and on the enhancement of the extraction was also found with the rate of oxidation of manganese(II) acetylacetonate complex (Fig. 5, Ref. 7) and cobalt(II) acetylacetonate complex (Fig. 5, Ref. 8) in an organic solvent.

There is no direct indication of the oxidant of iron(II) in the complex. The dissolved oxygen molecules in the solvent could be considered as this. However the fact that the rate of oxidation is not different when the organic phase is saturated by the air and when it is saturated by oxygen indicates that the reaction of the oxygen molecules or that of any species in an equilibrium with the oxygen molecules should not be the rate determining step except when the equilibrium is very favorable for these species. Furthermore, the independence of the rate on the concentration of benzoyltrifluoroacetone indicates that any reaction concerning with this β-diketone should not be the rate determining step.

Up to now no conclusion can be drawn about the rate determining step which explains the above two observations: the nearly identical rate of oxidation of the $\mathrm{Fe(bfa)_2}$ and $\mathrm{Fe(bfa)_2TOPO}$ species, and the slow oxidation of the iron(II) in the $\mathrm{Fe(bfa)_2(TOPO)_2}$ and in the $\mathrm{tba^+Fe(bfa)_3{}^-}$ species.

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