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Reduction of Manganese(III) in Tris(benzoyltrifluoroacetonato)Mn(III) in Carbon Tetrachloride in the Presence of Trioctylphosphine Oxide

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An addition of trioctylphosphine oxide (TOPO) enhanced the rate of back extraction of manganese in tris(benzoyltrifluoroacetonato)Mn(III) from carbon tetrachloride containing benzoyltrifluoroacetone (4,4,4-trifluoro-1-phenyl-1,3-butanedione, Hbfa) into acid aqueous solutions due to reduction of manganese(III) in this complex in the organic phase. It was found by spectrometry that manganese(III) in this complex in water- and air-saturated carbon tetrachloride was stable for a long time in the absence of TOPO but its reduction occurred in the presence of TOPO. The rate of reduction was first order with respect to the TOPO concentration and inverse first order with respect to the Hbfa concentration. This was explained as follows: An addition of TOPO to the metal ion in the complex promoted the dissociation of one of the bfa^- ions in the complex and the leaving bfa^- ion gave an electron to the manganese(III). On the other hand, a bfa^- ion from the coexisting Hbfa in the solution should exchange with the bfa^- in the $Mn^{III}(bfa)_3$ complex but it does not cause reduction of manganese(III) and this was assumed to compete with the addition of TOPO and to cause the inverse first order dependence of the rate of reduction on the Hbfa concentration.

It is known that some metal ions are oxidized during the solvent extraction from an aqueous solution where a lower oxidation state is more stable into an organic solvent where a higher oxidation state is more stable. In our laboratory, such oxidation reactions have been studied with manganese(II),[1] cobalt(II),[2] cerium(III),[3] and iron(II)[4] from the standpoint of kinetics and the rate of oxidation of metal ions extracted as a β-diketonate was found to be affected by several factors in the system. In theses studies, it was recognized that the rate of oxidation in the organic phase was slowed down by an addition of trioctylphosphine oxide (TOPO) which formed stable adducts with the extracted chelate of the metal ion in the lower oxidation state in the organic phase.

In the course of studies to learn the effect of such redox reactions on the solvent extraction behavior of metal ions, it was found that manganese(III) in the tris-complex with benzoyltrifluoroacetone (4,4,4-trifluoro-1-phenyl-1,3-butanedione, Hbfa) dissolved in carbon tetrachloride was back extracted by an agitation with acid aqueous solutions only slowly. This was assumed to be due to reduction of manganese(III) to manganese(II) which was not extractable with Hbfa from such acid aqueous solution and the slow back extraction was due to the fact that the reduction in the aqueous phase proceeded rather slowly. Furthermore, it was also found that the rate of this back extraction was enhanced by an addition of TOPO into the organic phase. Since only a very small amount of TOPO should distribute into the aqueous phase, this effect of TOPO was assumed to be due to reduction of manganese(III) in the complex in the organic phase which was caused by TOPO. In order to know the details of this reduction of manganese(III) in the complex in the organic phase, the rate of reduction in carbon tetrachloride solution was measured under several conditions.

Experimental

The experiments were made in a thermostated room at 298 K. All the reagents were of an analytical grade. The bis(acetylacetonato)-manganese(II), tris(acetylacetonato)manganese(III) (where acetylacetone is 2,4-pentanedione, Hacac), the benzoyltrifluoroacetone, and TOPO were obtained from Dojindo Laboratories. The Hbfa was purified by recrystallization from toluene. The TOPO was purified by recrystallization from cyclohexane. Sodium perchlorate was recrystallized three times from water. Deionized water was distilled and used. The carbon tetrachloride stock solution of bis(benzoyltrifluoroacetonato)manganese(II) ($Mn^{II}(bfa)_2$) and tris(benzoyltrifluoroacetonato)manganese(III) ($Mn^{III}(bfa)_3$) were prepared by the following ligand exchange method. A weighed amount of bis(acetylacetonato)manganese(II) ($Mn^{II}(acac)_2$) or tris(acetylacetonato)-manganese(III) ($Mn^{III}(acac)_3$) was dissolved in a water-saturated carbon tetrachloride solution containing an excess amount of Hbfa. The acetylacetonate ions in the complex were exchanged with benzoyltrifluoroacetonate ions by this procedure and two times or three times by molar concentration of Hacac to the metal ion are dissociated. The experiments of oxidation or reduction of the metal ions in the complexes in carbon tetrachloride solutions were made in stoppered glass tubes (capacity 20cm^3). The tube was always covered by aluminum foil in order to keep the sample in the dark during the experiments.

The oxidation of manganese(II) in $Mn^{II}(bfa)_2$ in water- and air-saturated carbon tetrachloride was studied as follows. A carbon tetrachloride solution of $Mn^{II}(bfa)_2$ complex prepared just before the experiments was placed in a tube and none or an amount of carbon tetrachloride solution of TOPO was added. The sample was left standing for a certain time and the optical absorption was measured at 430 nm by using quartz cells of 1 cm light path and a spectrophotometer (Hitachi U-3410). The $Mn^{III}(bfa)_3$ complex has an absorption at this wavelength (the molar absorption coefficient was $\varepsilon = 1.9 \times 10^3$) but the $\mathrm{Mn^{II}(bfa)_2}$ complex has negligible absorption. The reduction of manganese(III) in $\mathrm{Mn^{III}(bfa)_3}$ in a carbon tetrachloride solution which was thus prepared was determined from the optical absorption which was measured in a similar manner as above except that $\mathrm{Mn^{III}(bfa)_3}$ was present in the initial solution. The initial concentration of $\mathrm{Mn^{III}(bfa)_3}$ in carbon tetrachloride was 1×10^{-3} mol dm^{-3}.

The rate of back extraction of manganese from an organic solution containing $\mathrm{Mn^{III}(bfa)_3}$ and none or an amount of TOPO was measured as follows. The organic solution was placed in a tube and the same volume of aqueous chloride solution containing 0.9 mol dm^{-3} sodium chloride and 0.1 mol dm^{-3} hydrochloric acid was added. The two phases were agitated for a certain time and separated. The manganese which still remained in the organic phase was stripped by 1 mol dm^{-3} hydrochloric acid. The amount of manganese in the aqueous phase and that thus stripped from the organic phase were determined by an atomic absorption method.

The two-phase distribution experiments of manganese in the organic solution which initially contained $\mathrm{Mn^{III}(bfa)_3}$, Hbfa, and TOPO, and was left standing for one week were conducted in a similar manner to that described above, except that the two-phases were agitated for 20 min. This was enough to establish the two-phase distribution equilibrium.

Statistical

In the present paper, any chemical species in an organic solution is denoted by the subscript "org" while that in an aqueous solution is denoted by no subscript. The volumes of the organic and aqueous phase are assumed to be the same.

The rate of reduction of manganese(III) in the $\mathrm{Mn^{III}(bfa)_3}$ complex in an organic solution can be given as:

$$\begin{aligned} v &= -\mathrm{d[Mn(III)]_{org}}/\mathrm{d}t \\ &= k\mathrm{[Mn(III)]_{org}[Hbfa]_{org}^{a}[TOPO]_{org}^{b}}\cdots, \end{aligned} \tag{1}$$

$$-\mathrm{d[Mn(III)]_{org}/[Mn(III)]_{org}} = k\mathrm{[Hbfa]_{org}^{a}[TOPO]_{org}^{b}}\cdots \mathrm{d}t. \tag{2}$$

By integrating Eq. 2, the following equation is obtained.

$$\ln\ \mathrm{[Mn(III)]_{org}} = -k_{\mathrm{obsd}}t + C_0. \tag{3}$$

Here, k_{obsd} is the observed rate constant which can be written as:

$$k_{\mathrm{obsd}} = k\mathrm{[Hbfa]_{org}^{a}[TOPO]_{org}^{b}}\cdots. \tag{4}$$

The value of C_0 is equal to $\ln\ \mathrm{[Mn(III)]_{org,init}}$ when t=0.

Thus, from Eq. 3, the following equation can be obtained:

$$\log\ (\mathrm{[Mn(III)]_{org}/[Mn(III)]_{org,init}}) = -(k_{\mathrm{obsd}}/2.303)t. \tag{5}$$

The value of k_{obsd} can be obtained from the slope of the $\log\ (\mathrm{[Mn(III)]_{org}/[Mn(III)]_{org,init}})$ vs. t plot. The rate of oxidation may be written in a similar way if Mn(III) in the equations is replaced by Mn(II).

The complex formation of manganese(II) with Hbfa in a solvent extraction system in the absence of TOPO can be written as:

$$\begin{aligned} &\mathrm{Mn^{2+}} + n\mathrm{bfa^{-}} \rightleftharpoons \mathrm{Mn(bfa)}_n^{2-n}, \\ &\beta_n = [\mathrm{Mn(bfa)}_n^{2-n}][\mathrm{Mn^{2+}}]^{-1}[\mathrm{bfa^{-}}]^{-n}. \end{aligned} \tag{6}$$

Among the metal complexes, only $\mathrm{Mn(bfa)_2}$ should be extracted;

$$\begin{aligned} &\mathrm{Mn(bfa)_2} \rightleftharpoons \mathrm{Mn(bfa)_{2(org)}} \\ &K_{\mathrm{dm}} = \mathrm{[Mn(bfa)_2]_{org}/[Mn(bfa)_2]}. \end{aligned} \tag{7}$$

The distribution ratio, D_0, can be written as

$$\begin{aligned} D_0 &= \frac{\mathrm{[Mn(bfa)_2]_{org}}}{\mathrm{[Mn^{2+}] + [Mn(bfa)^{+}] + [Mn(bfa)_2]} + \cdots} \\ &= K_{\mathrm{dm}}\beta_2[\mathrm{bfa^{-}}]^2 / \left(1 + \sum \beta_n[\mathrm{bfa^{-}}]^n\right). \end{aligned} \tag{8}$$

The concentration, $[\mathrm{bfa^{-}}]$, can be obtained from the initial Hbfa concentration in the organic phase, the hydrogen-ion concentration in the aqueous phase at equilibrium, the distribution constant, K_{d}, and acid dissociation constant, K_{a}, of Hbfa as was given in the previous paper.[5] In the presence of TOPO, the $\mathrm{Mn^{II}(bfa)_2}$ complex may form adducts with this solvating type ligand:

$$\begin{aligned} &\mathrm{Mn(bfa)_{2(org)}} + n\mathrm{TOPO_{(org)}} \rightleftharpoons \mathrm{Mn(bfa)_2(TOPO)}_{n\mathrm{(org)}} \\ &\beta_{(\mathrm{org})n} = [\mathrm{Mn(bfa)_2(TOPO)}_n]_{\mathrm{org}}\mathrm{[Mn(bfa)_2]_{org}^{-1}[TOPO]}_{\mathrm{org}}^{-n}. \end{aligned} \tag{9}$$

When the adducts with TOPO are formed, the distribution ratio should be written as:

$$\begin{aligned} D &= \frac{\mathrm{[Mn(bfa)_2]_{org} + [Mn(bfa)_2(TOPO)]_{org} + [Mn(bfa)_2(TOPO)_2]_{org}}}{\mathrm{[Mn^{2+}] + [Mn(bfa)^{+}] + [Mn(bfa)_2]} + \cdots} \\ &= \frac{K_{\mathrm{dm}}\beta_2[\mathrm{bfa^{-}}]^2(1 + \beta_{(\mathrm{org})1}[\mathrm{TOPO}] + \beta_{(\mathrm{org})2}[\mathrm{TOPO}]^2)}{1 + \sum \beta_n[\mathrm{bfa^{-}}]^n}. \end{aligned} \tag{10}$$

Under the conditions where the extraction of manganese(II) with Hbfa into the organic phase is negligible but the extraction of manganese(III) is nearly quantitative and thus the manganese species is predominantly $\mathrm{Mn^{2+}}$ in the aqueous phase, the distribution ratio can be written as:

$$D = \frac{\mathrm{[Mn^{III}(bfa)_3]_{org}}}{\mathrm{[Mn^{2+}]}}. \tag{11}$$

When the manganese(III) complex is back-extracted by agitation with an aqueous solution, the rate can be represented as:

$$v = -\mathrm{d[Mn(III)]_{org}}/\mathrm{d}t = k\mathrm{[Mn(III)]_{org}[A]^{a}[B]^{b}}\cdots, \tag{12}$$

$$\ln\ \mathrm{[Mn(III)]_{org}} = -k_{\mathrm{obsd}} + C_0, \tag{13}$$

where each A, B, $\cdots$ is a certain material in the system and k_{obsd} is the observed rate constant defined as $k_{\mathrm{obsd}} = k\mathrm{[A]^{a}[B]^{b}}\cdots$. Thus the following equation is obtained:

$$\log\ (\mathrm{[Mn(III)]_{org}/[Mn(III)]_{org,init}}) = -(k_{\mathrm{obsd}}/2.303)t. \tag{14}$$

Results

It was reported that manganese(II) could be extracted with Hbfa in carbon tetrachloride.[5] In the present study, it was found by spectrophotometry that the extracted $\mathrm{Mn^{II}(bfa)_2}$

species in the carbon tetrachloride solution did not change by letting the solution stand for at least one week. Thus, the oxidation of manganese(II) in $Mn^{II}(bfa)_2$ to manganese(III) in carbon tetrachloride was concluded to be negligible.

When carbon tetrachloride containing $Mn^{III}(bfa)_3$ and 0.1 $mol\,dm^{-3}$ Hbfa was agitated with the same volume of an aqueous solution containing 0.9 $mol\,dm^{-3}$ sodium chloride and 0.1 $mol\,dm^{-3}$ hydrochloric acid for a short time, a very small part of the manganese was stripped. When the two-phase agitation was further continued, the amount of manganese stripped increased gradually. Figure 1(a) gives the change in the distribution ratio as a function of the two-phase agitation time. Since the manganese(III) in the complex in the organic phase is rather stable and only a very small amount of manganese(III) is back-extracted, the back extraction should be due to reduction of manganese(III) in the aqueous phase. Thus the distribution ratio should be given by Eq. 11. Similar results were obtained in the previous study when the organic phase contained $Mn^{III}(acac)_3$.[1] However, the rate of back extraction is much higher with $Mn^{III}(bfa)_3$ than with $Mn^{III}(acac)_3$. It is also seen from Fig. 1(a) that the rate of back-extraction is much higher when the organic phase also contains 0.1 $mol\,dm^{-3}$ TOPO. Since the back-extraction of $Mn^{III}(bfa)_3$ is slow, the faster back extraction in the presence of TOPO should be caused by reduction of manganese(III) to manganese(II) in the organic phase.

The rate of back extraction can be written by Eqs. 12, 13, and 14. The results in Fig. 1(a) were treated by these equations. Figure 1(b) gives the plot on the basis of Eq. 14. The value of k_{obsd} was obtained from the slope to be $10^{-3.8}$ in the absence of TOPO and $10^{-3.5}$ in the presence of 0.1 $mol\,dm^{-3}$ TOPO in the organic phase.

On the basis of these results which indicated that TOPO should promote the reduction of manganese(III) in the $Mn^{III}(bfa)_3$ chelate in the organic phase, the reduction of manganese(III) was further studied with organic solutions containing $Mn^{III}(bfa)_3$, Hbfa, and TOPO and saturated with water and air but contacted with no aqueous solution. The color of carbon tetrachloride solution containing $Mn^{III}(bfa)_3$ and Hbfa was brown and the absorption at 430 nm was constant for a long time in the absence of TOPO, for example, for 3 h. However, when the organic phase contained TOPO, the absorption decreased gradually. This was concluded to be due to the reduction of $Mn^{III}(bfa)_3$ and this should produce the $Mn^{II}(bfa)_2(TOPO)_n$ species (*n* is one or two) in the organic solution as was described in Ref. 5. On the other hand, it is assumed that in this carbon tetrachloride solution, $Mn^{III}(bfa)_3$ may not form stable adducts with TOPO molecules. This is because there are no coordination sites to accept TOPO on the central metal ion in the six coordinated $Mn^{III}(bfa)_3$ chelate but the $Mn^{II}(bfa)_2$ chelate should be four coordinated and can accept at maximum two TOPO molecules. As it was pointed out, Hbfa and TOPO partially associate in water-saturated carbon tetrachloride and the following equilibrium was reported:[6]

$$Hbfa_{(org)} + TOPO_{(org)} \rightleftharpoons Hbfa{\cdot}TOPO_{(org)}$$

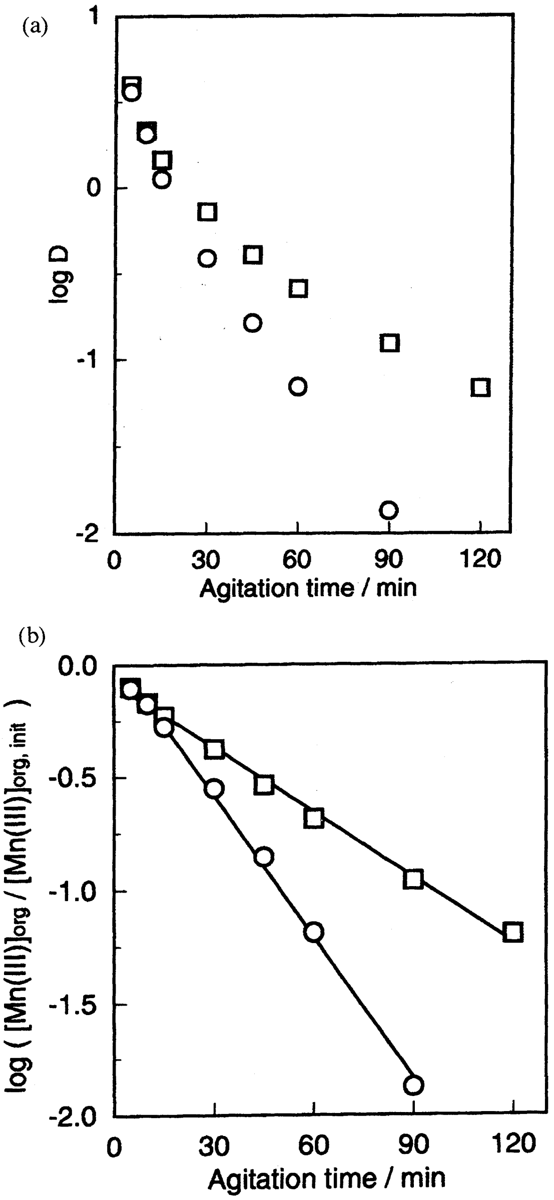

Fig. 1. The rate of back-extraction of manganese in CCl_4 which contains $Mn^{III}(bfa)_3$ as a function of the agitation time with aqueous phase containing 0.1 $mol\,dm^{-3}$ HCl and 0.9 $mol\,dm^{-3}$ NaCl. The organic phase contained only 0.1 $mol\,dm^{-3}$ Hbfa (□) and both Hbfa and TOPO at 0.1 $mol\,dm^{-3}$ (○). (a); the data are given by the distribution ratio, (b); the data are given by the decrease in the manganese(III), cf. Eqs. 5, 11, and 14.

$$K_{as} = [Hbfa{\cdot}TOPO]_{org}[Hbfa]_{org}^{-1}[TOPO]_{org}^{-1}. \qquad (15)$$

Since the Hbfa and TOPO are in a large excess to the metal ion, the decrease in the concentration of Hbfa and TOPO due to the association with the metal ions should be negligible. Thus, the following equations can be written:

$$[Hbfa]_{org,total} = [Hbfa]_{org} + [Hbfa{\cdot}TOPO]_{org} \qquad (16)$$

$$[TOPO]_{org,total} = [TOPO]_{org} + [Hbfa{\cdot}TOPO]_{org}. \qquad (17)$$

The free concentration of Hbfa and TOPO can be calculated on the basis of Eqs. 15, 16, and 17 by introducing the value $K_{as}=10^{0.59}$ in Ref. 6. For example, when the concentration of both reagents is 0.1 mol dm^{-3}, a 23% portion of the both should be in the form of the associate, Hbfa•TOPO. For precise calculations of these data, this type of association of the two reagents which decreases the free concentrations should be taken into account.

Figure 2 gives examples of data of the changes in the $\mathrm{Mn^{III}(bfa)_3}$ concentration in carbon tetrachloride solutions while they were standing. They were calculated from the results of spectrophotometric measurements. The data are given by the $\log([\mathrm{Mn(III)}]_{\mathrm{org}}/[\mathrm{Mn(III)}]_{\mathrm{org,init}})$ vs. t plot on the basis of Eq. 5. As is seen from Fig. 2, the line is steeper when the TOPO concentration is higher. This indicates that the rate of reduction is higher when the TOPO concentration is higher. The values of k_{obsd} were obtained from these slopes and also from other results on the basis of Eq. 5. The value of $\log k_{\mathrm{obsd}}$ is given in Fig. 3 as a function of the free TOPO concentration which was calculated on the basis of Eqs. 15, 16, and 17 by using the value $K_{as}=10^{0.59}$ for the correction of free TOPO and Hbfa concentrations. As is seen from Fig. 3, the value of k_{obsd} is first order dependent on the TOPO concentration.

Figure 4 gives the $\log([\mathrm{Mn^{III}(bfa)_3}]_{\mathrm{org}}/[\mathrm{Mn^{III}(bfa)_3}]_{\mathrm{org,init}})$ vs. t plot when the initial concentration of TOPO is 1×10^{-3} mol dm^{-3} and the initial Hbfa concentration is 5×10^{-3} to 0.1 mol dm^{-3}. The free concentration of Hbfa and TOPO were also obtained in a similar manner as above. As is seen from Fig. 4, the plot is steeper when the Hbfa concentration is lower. Thus, the reduction is slower when the Hbfa concentration is higher. The values of k_{obsd} obtained from the slope of the lines in Fig. 4 and from other results are plotted as function of the Hbfa concentration at equilibrium which is calculated on the basis of Eqs. 15, 16, and 17 by using the value of K_{as} in Fig. 5.

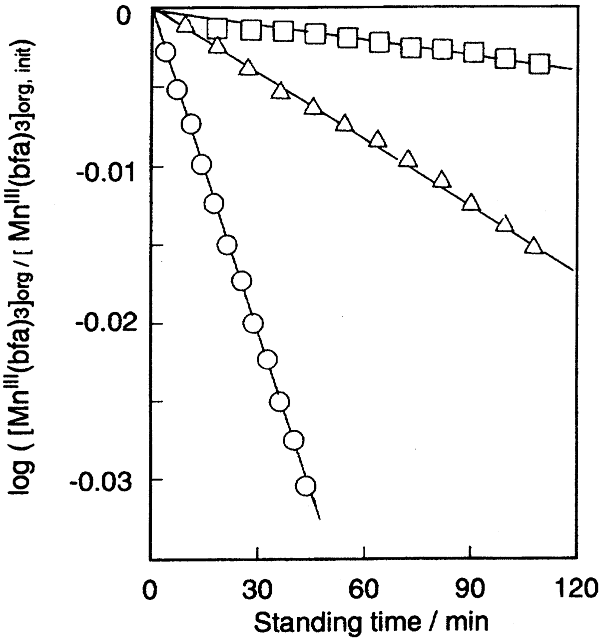

Fig. 2. Decrease in $\mathrm{Mn^{III}(bfa)_3}$ concentration in $\mathrm{CCl_4}$ initially containing 0.1 mol dm^{-3} Hbfa and 2×10^{-3} (□), 5×10^{-3} (△), or 2×10^{-2} (○) mol dm^{-3} TOPO as a function of the standing time. cf. Eq. 5. $[\mathrm{Mn^{III}(bfa)_3}]_{\mathrm{org,init}}$ is 1×10^{-4} mol dm^{-3}.

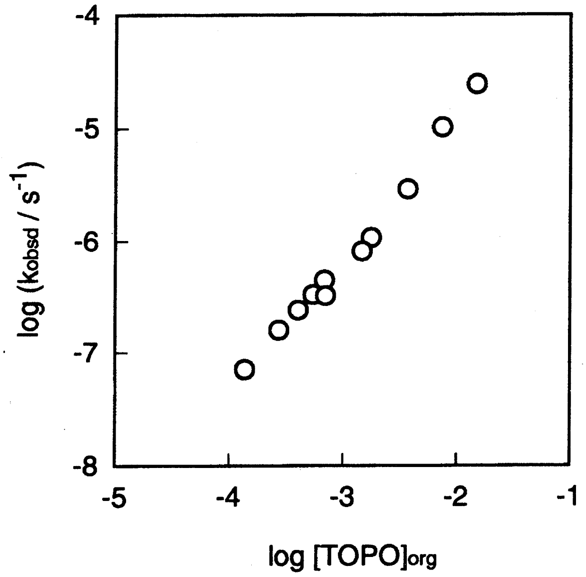

Fig. 3. Dependence of the observed rate constant of reduction of $\mathrm{Mn^{III}(bfa)_3}$ in Eq. 4 in $\mathrm{CCl_4}$ initially containing 0.1 mol dm^{-3} Hbfa and 1×10^{-4} to 2×10^{-2} mol dm^{-3} TOPO.

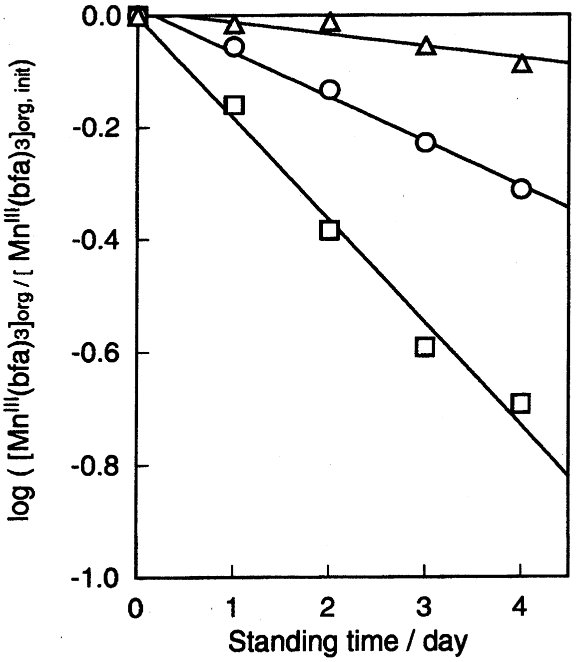

Fig. 4. Decrease in $\mathrm{Mn^{III}(bfa)_3}$ concentration in $\mathrm{CCl_4}$ initially containing 1×10^{-3} mol dm^{-3} TOPO and 2×10^{-2} (□), 5×10^{-2} (○), or 1×10^{-1} (△) mol dm^{-3} Hbfa as a function of the standing time. cf. Eq. 5. $[\mathrm{Mn^{III}(bfa)_3}]_{\mathrm{org,init}}$ is 1×10^{-4} mol dm^{-3}.

As is seen from Fig. 5, the rate of reduction is inversely first order with respect to the Hbfa concentration. If the effect of other solutes in the solution on the rate is assumed to be

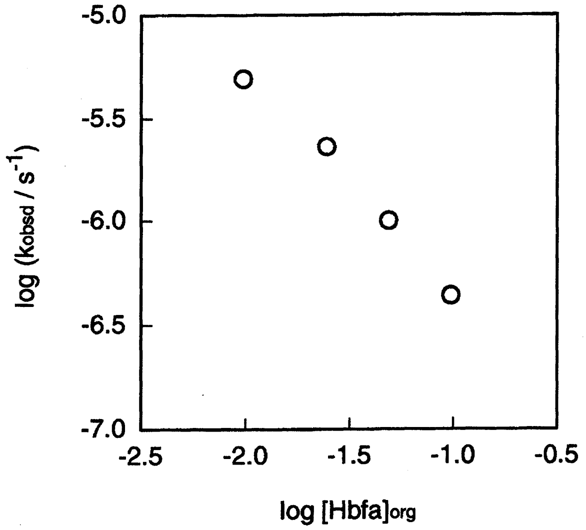

Fig. 5. Dependence of the observed rate constant of reduction of $Mn^{III}(bfa)_3$ in Eq. 4 in CCl_4 initially containing 1×10^{-3} mol dm^{-3} TOPO and 1×10^{-2} to 1×10^{-1} mol dm^{-3} Hbfa.

negligible, Eq. 1 can be written from the results in Figs. 3 and 5 as:

$$-\frac{d[Mn^{III}(bfa)_3]_{org}}{dt} = k[Mn^{III}(bfa)_3]_{org}[TOPO]_{org}[Hbfa]_{org}^{-1} \cdots \quad (18)$$

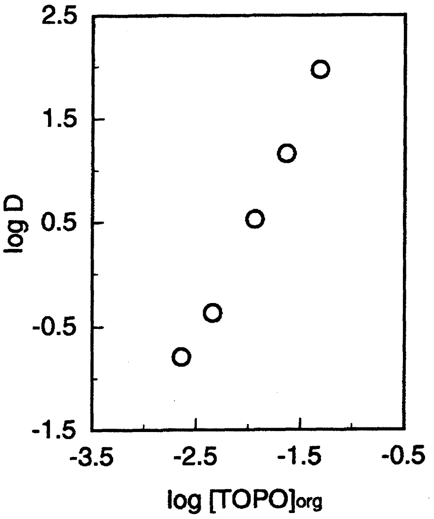

Fig. 6. Distribution ratio of manganese as a function of TOPO concentration. Org. phase; CCl_4 initially containing 1×10^{-4} mol dm^{-3} $Mn^{III}(bfa)_3$, 0.1 mol dm^{-3} Hbfa and TOPO at various concentrations of Hbfa and left standing for one week. Aqueous phase; 1 mol dm^{-3} NaCl containing an acetate buffer. The two phases were agitated for 20 min.

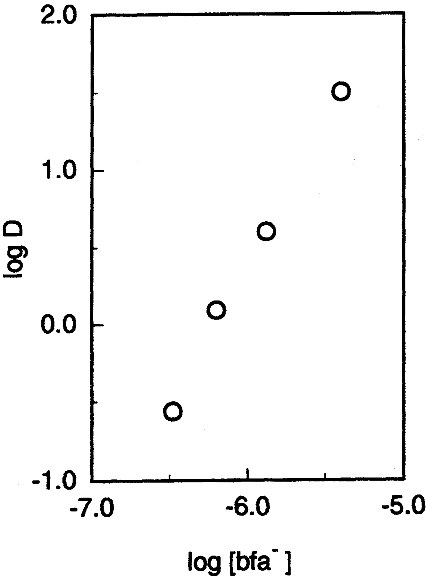

Fig. 7. Distribution ratio of manganese as a function of bfa$^-$ concentration. Org. phase; CCl_4 initially containing 1×10^{-4} mol dm^{-3} $Mn^{III}(bfa)_3$, 2×10^{-2} mol dm^{-3} TOPO and Hbfa at various concentrations of Hbfa and left standing for one week. Aqueous phase; 1 mol dm^{-3} NaCl containing an acetate buffer at pH 3.5. The two phases were agitated for 20 min.

In carbon tetrachloride solution containing TOPO, the reduction of manganese(III) in $Mn^{III}(bfa)_3$ to manganese(II) in $Mn^{II}(bfa)_2(TOPO)_n$ was further studied. Carbon tetrachloride solutions initially containing an amount of $Mn^{III}(bfa)_3$ and both Hbfa and TOPO at various concentrations were left standing for one week. It was observed that the optical absorption due to $Mn^{III}(bfa)_3$ became negligible. This indicates that the reduction of manganese(III) in the complex occurred quantitatively during the standing of the solutions. Furthermore, it was concluded that the oxidation of the manganese(II) species which had been produced from manganese(III) by the reduction in the organic solutions was negligible in the presence of TOPO. In order to confirm the chemical form of the manganese(II) species thus produced in the organic solution, a series of back-extraction experiments were carried out. The carbon tetrachloride solutions containing the manganese(II) complex thus obtained by the reduction of manganese(III) were agitated with the same volume of aqueous 1 mol dm^{-3} sodium chloride solutions at pH 3.5 for 20 min and the distribution ratio of manganese was measured. Figure 6 gives the results when the organic phase initially contained 0.1 mol dm^{-3} Hbfa and various concentrations of TOPO. Figure 7 gives the results when the organic phase initially contained 0.02 mol dm^{-3} TOPO and various concentrations of Hbfa. The bfa$^-$ concentration in Fig. 7 was calculated in a similar manner to that described in Ref. 5. As is seen from Figs. 6 and 7, the slope of the plot in both figures is +2. From these, the distribution ratio should be represented by D=$[Mn^{II}(bfa)_2(TOPO)_2]_{org}/[Mn^{2+}]$ as can be seen from Eq. 10; under these conditions, the effect of complex formation in the aqueous phase is negligible. The rate constant for the reduction of manganese(III) in the complex in water saturated carbon tetrachloride can be calculated from the data in Figs. 3 and 5 to be k=$k_{obsd}[TOPO][Hbfa]^{-1}$ and the value obtained is $10^{-4.3}$.

Discussion

In the present study, $Mn^{III}(bfa)_3$ in carbon tetrachloride was prepared by a ligand exchange method. The exchange of $acac^-$ in the initial $Mn^{III}(acac)_3$ in the carbon tetrachloride solution with bfa^- in Hbfa should be complete within the limit of experimental error. This was confirmed as follows. The equilibrium of the ligand exchange can be represented by;

$$Mn^{III}(acac)_{3(org)} + 3Hbfa_{(org)} \rightleftharpoons Mn^{III}(bfa)_{3(org)} + 3Hacac_{(org)}$$
$$K = [Mn^{III}(bfa)_3]_{org}[Hacac]^3_{org}[Mn^{III}(acac)_3]^{-1}_{org}[Hbfa]^{-3}_{org}. \tag{19}$$

As is seen from Eq. 19, if the ligand exchange would only be partial, the concentration $[Mn^{III}(bfa)_3]_{org}$ should be dependent on $[Hbfa]_{org}$. It was observed that the absorption spectrum due to $Mn^{III}(bfa)_3$ was not different within the experimental accuracy when $[Mn^{III}(acac)_3]_{org,init}$ was 1×10^{-3} mol dm^{-3} and $[Hbfa]_{org,init}$ was 5×10^{-3} to 0.1 mol dm^{-3}. The effect of released Hacac on the rate of reaction was concluded to be negligible from the results that the reaction rate was essentially the same even when the same amount of Hacac which should be released from the $Mn^{III}(acac)_3$ complex by the ligand exchange was further added to the sample solution and thus the concentration of Hacac was doubled.

When no TOPO was present, both $Mn^{II}(bfa)_2$ and $Mn^{III}(bfa)_3$ were stable for a long time during the standing of the carbon tetrachloride solution saturated with water and air and containing a large excess of Hbfa. This should be because the rate of oxidation of $Mn^{II}(bfa)_2$ and/or the rate of reduction of $Mn^{III}(bfa)_3$ is very low. On the other hand, it was found in the previous studies[1,8] that the chelate complexes, $Mn^{II}A_2$, where A^- was acetylacetonate, benzoylacetonate, or dibenzoylacetonate ion, oxidized rather rapidly in water- and air-saturated carbon tetrachloride. The oxidation was found to be nearly quantitative after keeping the solution for a long time. Thus the rate of oxidation seems to be lower when the β-diketonate ion has a CF_3– group than when it has none. In other words, the rate of oxidation of the central metal ion in the β-diketonate complexes in nonpolar organic solutions seems to be slower if the stability of the corresponding metal complex in aqueous solutions is lower.

The results in Fig. 1(a) that manganese(III) in $Mn^{III}(bfa)_3$ in the carbon tetrachloride solution is gradually back-extracted when the solution is agitated with the acid aqueous solution suggest that $Mn^{III}(bfa)_3$ is reduced in the aqueous phase even in the absence of TOPO. This is because the distribution constant of the $Mn^{III}(bfa)_3$ ($K_{dm} = [Mn^{III}(bfa)_3]_{org}/[Mn^{III}(bfa)_3]$) should be much higher than that of $Mn^{II}(bfa)_2$. The latter was reported to be $10^{1.73}$ under similar conditions.[5] From the reported values[5] K_{ex} ($= [Mn^{II}(bfa)_2]_{org}[H^+]^2[Mn^{2+}]^{-1}[Hbfa]^{-2}_{org}$) is $10^{-12.62}$ and the adduct formation constant in Eq. 9 is $10^{6.1}$ for $\beta_{(org)1}$ and $10^{10.4}$ for $\beta_{(org)2}$, it can be calculated that the distribution ratio of manganese(II) when $[Hbfa]_{org}$ is 0.1 mol dm^{-3} in the system in Fig. 1(a), is less than 10^{-12} and in the presence of 0.1 mol dm^{-3} of TOPO, it is still less than 10^{-4}. From these, it can be concluded that only negligible amounts of manganese(II) produced by the reduction should be extracted from the aqueous phase to the organic phase. The distribution in Fig. 1(a) should be represented by Eq. 11 where $[Mn(bfa)_3]_{org} = [Mn(bfa)_3]_{org,init} - [Mn^{2+}]$ if the amount of manganese(III) in the aqueous phase is assumed to be negligible. The decrease in D in Fig. 1(a) as a function of the agitation time becomes smaller as the time becomes longer. The slope of the plot of results of the two experiments in Fig. 1(a) changes. This does not indicate that the rate of backward reaction increased and the system is approaching a stationary state. Figure 1(b) gives the plot on the basis of Eq. 14, which is calculated from the data in Fig. 1(a) on the basis of Eq. 12. It is seen from Fig. 1(b) that each plot is a straight line throughout all the time, and thus, the backward reaction should be negligible even after the two-phase agitation for a long time.

In the previous paper,[1] the oxidizing reagent for the manganese(II) in the bis(acetylacetonato)manganese(II) in carbon tetrachloride was assumed to be the dissolved oxygen from the air. The same can be assumed if oxidation would occur in the present study. On the other hand, the reduction of manganese(III) in the $Mn^{III}(bfa)_3$ complex occurred in the absence of any effective reductant. In this case, the most probable reducing reagent should be the leaving bfa^-, as was assumed with the reduction of cobalt(III) in tris(acetylacetonato)cobalt(III) in carbon tetrachloride–aqueous perchlorate systems during a prolonged two-phase agitation.[7] It should give one electron to the metal ion in the complex and the bfa^- should be oxidized and become, for example, a carboxylic acid as was assumed in Ref. 7.

When the $Mn^{III}(bfa)_3$ complex in carbon tetrachloride solution in the presence of TOPO was reduced, the final product should be in the form of $Mn^{II}(bfa)_2(TOPO)_2$ as is seen from the results in Figs. 6 and 7. This agrees with the assumption from the association constants of $Mn^{II}(bfa)_2$ with TOPO.[5] It can be estimated from these constants that even in the lowest TOPO concentration in Fig. 3, 1×10^{-3} mol dm^{-3}, the molar ratio ($[Mn(bfa)_2(TOPO)_2]_{org}/[Mn(bfa)_2]_{org}$) can be calculated to be $10^{4.4}$ on the basis of Eq. 9 by using the values of $\beta_{(org)1}$ and $\beta_{(org)2}$.

It is seen from Figs. 2 and 4, that the reduction of manganese(III) in $Mn^{III}(bfa)_3$ occurs when TOPO is added to the solution of $Mn^{III}(bfa)_3$. The reduction of $Mn^{III}(bfa)_3$ in carbon tetrachloride is promoted by TOPO but it is interfered with by the coexisting Hbfa. Thus, TOPO and Hbfa causes just the inverse effect on the rate of reduction of $Mn^{III}(bfa)_3$. This may be explained as follows. In the absence of TOPO but the presence of an excess amount of Hbfa, it should be possible that an Hbfa molecule associates with the metal ion in the complex and the exchange of one bfa^- in the complex with that in Hbfa in the carbon tetrachloride solution may occur. However, this should not cause any reduction of the central metal ion, manganese(III), and this can not be recognized during the experiments of the present study. On the other hand, in the presence of TOPO, an addition of a TOPO molecule to the metal ion in the $Mn^{III}(bfa)_3$ chelate may occur and it may cause the dissociation of a bfa^- ion from the complex. If the leaving bfa^- gives an electron to the central metal ion, the metal ion should be reduced to manganese(II) and the final form of the complex should be $\mathrm{Mn^{II}(bfa)_2(TOPO)}_n$ where n is one or two. This should be the reason why the rate is first order with respect to the TOPO concentration. However, the product from the leaving $\mathrm{bfa^-}$, which gave an electron to the metal ion and thus should be oxidized, was not confirmed experimentally. On the other hand, as is assumed above, when the $\mathrm{bfa^-}$ of the complex is exchanged with the $\mathrm{bfa^-}$ of Hbfa, the rate should be proportional to the concentration of Hbfa. Thus, when such an exchange of $\mathrm{bfa^-}$ occurs, the entering $\mathrm{bfa^-}$ interfere with the addition of TOPO on the central manganese(III) ion. This should be the reason why the rate is inverse first order dependent on the Hbfa concentration in the solution.

It was described in the previous paper[1] that the rate of oxidation of manganese(II) in the bis(acetylacetonato)-manganese(II) in carbon tetrachloride was lowered by an addition of TOPO. Furthermore, it was found that when tris(acetylacetonato)Mn(III) was dissolved in carbon tetrachloride containing TOPO, the absorbance due to this complex decreased gradually. Although no further experiments were made in this previous work, it was assumed that the manganese(III) in the complex was reduced in the presence of TOPO. This should be caused by a similar reaction, as is found in the present study. However, it was not clearly described in this previous paper if this reduction of manganese-(III) in the complex by TOPO is the reason for the lowering of the rate of oxidation of manganese(II) in the complex by TOPO.

In the present study, the extracted species of manganese-(II) with Hbfa in the presence of TOPO was nearly all in the form of $\mathrm{Mn^{II}(bfa)_2(TOPO)_2}$. This indicates that $\mathrm{Mn^{II}(bfa)_2}$ in carbon tetrachloride is much more stable in the form of the adduct with TOPO in such a nonpolar organic solvent. It is still not known whether $\mathrm{Mn^{II}(bfa)_2}$ or $\mathrm{Mn^{III}(bfa)_3}$ is more thermodynamically stable in carbon tetrachloride solutions saturated with air and water. However, even if $\mathrm{Mn^{III}(bfa)_3}$ would be more stable than $\mathrm{Mn^{II}(bfa)_2}$ in such a nonpolar organic solvent, the adduct formation of $\mathrm{Mn^{II}(bfa)_2}$ with TOPO should make this lower oxidation state in the complex more stable. This should be the reason why the addition of TOPO caused the reduction of manganese(III) in the $\mathrm{Mn^{III}(bfa)_3}$ complex in carbon tetrachloride saturated by air and water.

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