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Rate of Back-Extraction of Tris(acetylacetonato)- and Tris(trifluoroacetylacetonato)chromium(III) from Carbon Tetrachloride into Aqueous Acid Perchlorate Solutions

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The rate of back-extraction of tris(acetylacetonato)chromium(III) ([Cr(acac)$_3$]), and tris(trifluoroacetylacetonato)chromium(III) ([Cr(tfa)$_3$]), from carbon tetrachloride into aqueous acid perchlorate solutions was measured. The rate of [Cr(acac)$_3$] was much higher and that of [Cr(tfa)$_3$] was also a little higher in the higher acid concentration range. This was concluded to be due to formation of the [Cr(acac)$_3$(H$^+$)$_2$] and the [Cr(tfa)$_3$H$^+$] species which increased the concentration of the tris-complex species in the aqueous phase. With the both complexes, the rate was not affected by the ligand concentration in the aqueous phase. From these results, the controlling reaction was concluded to be the dissociation of the first ligand from the tris-complex or from the proton associate of the tris-complex in the aqueous phase.

The rate of solvent extraction of chromium(III) as a non-charged chelate complex into a non-polar solvent is, in many cases, extremely low. This is due to that the rate of formation of extractable metal complex in the aqueous phase from the hydrated metal ions is extremely low.[1] The back-extraction of the extracted chromium(III) complex in the organic phase into the aqueous phase is also very slow in such systems. This should be due to that the dissociation of the ligands from the complex in the aqueous phase is very slow. However, up to now, only a few systematic kinetic studies seem to have been made on such slow back-extraction of metal complexes due to slow chemical reactions.[2–4]

In the present study, the rate of back-extraction of tris-complex of chromium(III) with acetylacetone (2,4-pentanedione) (Hacac), and trifluoroacetylacetone (1,1,1-trifluoro-2,4-pentanedione) (Htfa), from carbon tetrachloride into aqueous acid perchlorate solutions was measured under various experimental conditions and the mechanism of this process was considered.

Statistical

In the present paper, any chemical species in the organic phase is denoted by the subscript "org" while that in the aqueous phase is denoted by lack of subscript. The volume of the two phases is always assumed to be the same.

When an organic solvent containing a tris-complex, CrA$_3$, and the β-diketone, HA, is agitated with an aqueous solution, the CrA$_3$ species and the β-diketone in the organic phase transfer into the aqueous phase. The distribution equilibrium of this species and the reagent given by the following equations should be established within a short time.

$$\mathrm{CrA_3(org)} \rightleftarrows \mathrm{CrA_3}$$
$$K_{\mathrm{dm}} = [\mathrm{CrA_3}]_{\mathrm{org}}/[\mathrm{CrA_3}] \tag{1}$$

$$\mathrm{HA(org)} \rightleftarrows \mathrm{HA}$$
$$K_{\mathrm{d}} = [\mathrm{HA}]_{\mathrm{org}}/[\mathrm{HA}] \tag{2}$$

The distribution ratio, $D=[\mathrm{Cr(III)}]_{\mathrm{org}}/[\mathrm{Cr(III)}]$, in this stage should be similar to K_{dm} in Eq. 1 because the dissociation of ligands from the CrA$_3$ species hardly occurs within a short time. Thus the species Cr^{3+}, CrA^{2+}, and CrA$_2^+$ should be negligible in this period and these can be omitted from the equation.

When the CrA$_3$ species in the aqueous phase associates with one or two protons, the equilibrium and the distribution ratio may be written as;

$$\mathrm{CrA_3} + n\mathrm{H^+} \rightleftarrows \mathrm{CrA_3(H^+)}_n$$
$$\beta_{\mathrm{pr}(n)} = [\mathrm{CrA_3(H^+)}_n]/([\mathrm{CrA_3}][\mathrm{H^+}]^n) \tag{3}$$

$$\begin{aligned} D &= [\mathrm{CrA_3}]_{\mathrm{org}}/([\mathrm{CrA_3}]+[\mathrm{CrA_3(H^+)}]+[\mathrm{CrA_3(H^+)_2}]\cdots) \\ &= K_{\mathrm{dm}}/(1+\beta_{\mathrm{pr1}}[\mathrm{H^+}]+\beta_{\mathrm{pr2}}[\mathrm{H^+}]^2\cdots) \end{aligned} \tag{4}$$

If the rate of back-extraction, V_{bex}, is dependent on $[\mathrm{CrA_3}]_{\mathrm{org}}$, $[\mathrm{A^-}]$, and $[\mathrm{H^+}]$, the following equation can be written;

$$\begin{aligned} V_{\mathrm{bex}} &= -\mathrm{d}[\mathrm{CrA_3}]_{\mathrm{org}}/\mathrm{d}t \\ &= k_{\mathrm{bex,obsd}}\,[\mathrm{CrA_3}]_{\mathrm{org}} \\ &= k_{\mathrm{bex0}}[\mathrm{CrA_3}]_{\mathrm{org}}[\mathrm{A^-}]^a + k_{\mathrm{bex1}}[\mathrm{CrA_3}]_{\mathrm{org}}[\mathrm{A^-}]^{a'}[\mathrm{H^+}] \\ &\quad + k_{\mathrm{bex2}}[\mathrm{CrA_3}]_{\mathrm{org}}[\mathrm{A^-}]^{a''}[\mathrm{H^+}]^2\cdots \end{aligned} \tag{5}$$

Here, the value $k_{\mathrm{bex}(n)}$ is the rate constant for the unit reaction which is dependent on $[\mathrm{H^+}]^n$, and the value $k_{\mathrm{bex,obsd}}$ is the observed rate constant which can be related with the rate constant as;

$$\begin{aligned} k_{\mathrm{bex,obsd}} &= k_{\mathrm{bex0}}[\mathrm{A^-}]^a + k_{\mathrm{bex1}}[\mathrm{A^-}]^{a'}[\mathrm{H^+}] \\ &\quad + k_{\mathrm{bex2}}[\mathrm{A^-}]^{a''}[\mathrm{H^+}]^2\cdots \end{aligned} \tag{6}$$

where a, a', a'' is the order of dependence of rate with respect to $[\mathrm{A^-}]$.

By integrating Eq. 5, the following equation can be obtained:

$$\log([\mathrm{CrA_3}]_{\mathrm{org}}/[\mathrm{CrA_3}]_{\mathrm{org,init}}) = -k_{\mathrm{bex,obsd}}\,t/2.303 \tag{7}$$

As is seen from Eqs. 6 and 7, $k_{\mathrm{bex,obsd}}$ can be calculated from the $\log([CrA_3]_{org}/[CrA_3]_{org,init})$ vs. t plot. Furthermore, the value of the dependence on $[A^-]$ can be obtained from the slope of the $\log k_{bex,obsd}$ vs. $\log[A^-]$ plot when the other component is kept constant.

Since the rate of ligand dissociation from the CrA_3 species in the aqueous phase is low, one of the successive ligand dissociations could be the controlling reaction. Each of these unit reactions can be treated as follows.

It is possible that one or more than one chemical species are formed from the tris-complex by its association with protons in the aqueous phase. The rate constant for the ligand dissociation from these species could be different. Under such conditions, the rate of dissociation of the first ligand from the CrA_3 species should be written as:

$$V_{aq} = k_{aq0,obsd}[CrA_3] + k_{aq1,obsd}[CrA_3H^+] + k_{aq2,obsd}[CrA_3(H^+)_2] \quad (8)$$

It should be possible to write an equation in which the terms of each unit reaction are given in a general way. However, the following simpler equation can be written under the conditions of the present study. This is because no dependence of the rate on the A^- species was experimentally found and no term of the H^+ species is necessary in the rate equation when the terms of the protonated species are introduced as seen from Eq. 8.

$$V_{aq} = k_{aq0}[CrA_3] + k_{aq1}[CrA_3H^+] + k_{aq2}[CrA_3(H^+)_2] \quad (8')$$

By introducing Eq. 3, Eq. 8′ can be rewritten as:

$$\begin{aligned} V_{aq} &= k_{aq0}[CrA_3] + k_{aq1}\beta_{pr1}[CrA_3][H^+] + k_{aq2}\beta_{pr2}[CrA_3][H^+]^2 \\ &= (k_{aq0} + k_{aq1}\beta_{pr1}[H^+] + k_{aq2}\beta_{pr2}[H^+]^2)[CrA_3]_{org}/K_{dm} \end{aligned} \quad (9)$$

When one or more than one of these reactions control the whole process, the rate V_{bex} should be similar to the rate V_{aq}. From Eq. 5, Eq. 9 can be written as:

$$k_{bex,obsd} = (k_{aq0} + k_{aq1}\beta_{pr1}[H^+] + k_{aq2}\beta_{pr2}[H^+]^2)/K_{dm} \quad (10)$$

The rate of dissociation of the second ligand from the CrA_2^+ species or that of the third ligand from the CrA^{2+} species may be written as:

$$V'_{aq} = k'_{aq,obsd}[CrA_2^+]$$
$$V''_{aq} = k''_{aq,obsd}[CrA^{2+}]$$

As seen from the following equations which are obtained by similar treatments as above, the rate of back-extraction should be dependent on the ligand concentration in the aqueous phase if one or both of these process control the whole reaction.

$$k_{bex,obsd} = k'_{aq,obsd}\beta_2/(K_{dm}\beta_3[A^-]) \quad (10')$$

$$k_{bex,obsd} = k''_{aq,obsd}\beta_1/(K_{dm}\beta_3[A^-]^2) \quad (10'')$$

As seen from Eqs. 10, 10′, and 10″, if the value of the dependence on $[A^-]$ in Eq. 6 could be determined, the controlling reaction should be estimated. However, since no dependence of the rate on $[A^-]$ was always found in the present study, this problem will not be futher considered.

Here, β_n is the stability constant for the $CrA_n^{(3-n)+}$ species, that is, $\beta_n = [CrA_n^{(3-n)+}]/([Cr^{3+}][A^-]^n)$.

The concentration of β-diketone in the anionic form, $[A^-]$, can be calculated by using the distribution constant, K_d, and the acid dissociation constant, K_a, as:

$$[HA]_{org,init} = [HA]_{org} + [HA] + [A^-]$$
$$[A^-] = [HA]_{org,init}/(1 + (K_d + 1)K_a^{-1}[H^+]) \quad (11)$$

The values of K_d and pK_a for the β-diketones employed were $10^{0.2}$ and 10.1 for acetylacetone and $10^{0.4}$ and 6.6 for trifluoroacetylacetone under the conditions of the present study.[7–10)]

Experimental

All the regents were of an analytical grade. The tris(acetylacetonato)chromium(III) was supplied by Nacalai Tesque, Inc. The tris(trifluoroacetylacetonato)chromium(III) and acetylacetone were supplied by Tokyo Kasei Co. The trifluoroacetylacetone was supplied by Dojindo Lab. The sodium perchlorate was purified by recrystallization for three times from water. The carbon tetrachloride was washed several times with water before the use.

All the procedures were carried out in a thermostated room at 298 K. The aqueous phase was 4 mol dm^{-3} (H,Na)ClO$_4$ constant ionic media. Stoppered glass tubes (capacity 20 cm^3) were used for the back-extraction experiments. The carbon tetrachloride solution contained one of the tris-complexes and the β-diketone. A 6 cm^3 portion of this solution and the same volume of an aqueous acid perchlorate solution were place in the tube. The two phases were agitated for a certain time by a mechanical shaker. It was continued at maximum for two hours. However, a framework which rotated 20 times per minute was used for the two-phase agitation for a longer period than this. Under this two-phase agitation mode, the two phases were mixed up rather slowly but since the rate of reaction in this stage was very low, this was concluded to be enough to eliminate the effect of material transport. The two liquid phases were then centrifuged off. The total concentration of chromium(III) in the aqueous phase was measured by an atomic absorption method. The concentration of chromium(III) in the organic phase was calculated by subtracting this concentration from the initial concentration in the organic phase. The hydrogen-ion concentration in the aqueous phase at initial was measured by titration with a standard sodium hydroxide solution but when it was low, it was measured by a potentiometric method. The change in the $[H^+]$ during the experiments should be negligible under these conditions the hydrogen-ion concentration at initial can be regarded the same as that at pseudoequilibrium.

Results

When a carbon tetrachloride solution containing 0.01 mol dm^{-3} [Cr(acac)$_3$] and Hacac or 0.01 mol dm^{-3} [Cr(tfa)$_3$] and Htfa was agitated with 4 mol dm^{-3} (H,Na)ClO$_4$ aqueous solution where $[H^+]$ was 4 to 0.03 mol dm^{-3}, it was found that an amount of chromium(III) was back-extracted very rapidly and a pseudoequilibrium was established for the two-phase distribution of the chromium(III) species within 30 s. Figure 1 gives the $\log D$ vs. $\log[H^+]$ plot of back-extraction when

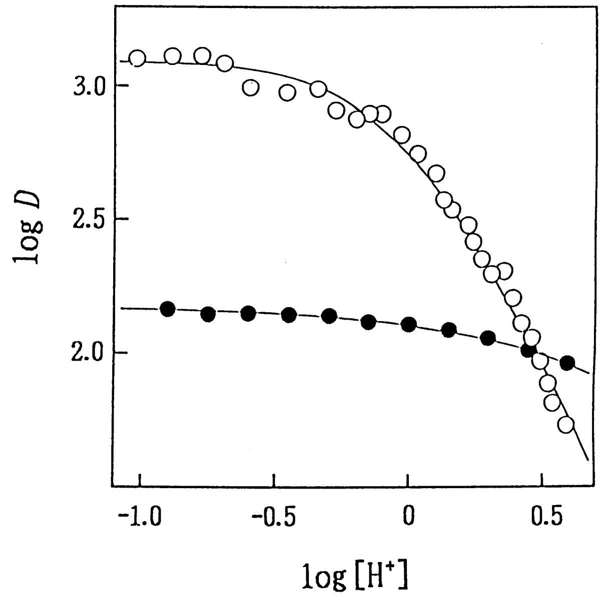

Fig. 1. Distribution ratio of chromium(III) after 30 s two-phase agitation in acetylacetonate system (open circles) and trifluoroacetylacetonate system (closed circles) as a function of the hydrogen-ion concentration. The solid curves are calculated by Eq. 4 which is introduced the values in Table 1.

Table 1. Values of Liquid-Liquid Distribution Constant (K_{dm} in Eq. 1) and Association Constant of the Tris-Complex with Protons ($\beta_{pr(n)}$ in Eq. 3); Org. phase: carbon tetrachloride; Aq. phase: 4 mol dm^{-3} perchlorate constant ionic media

	[Cr(acac)$_3$]	[Cr(tfa)$_3$]
log K_{dm}	3.1[a)]	2.2
log β_{pr1}	—[b)]	−0.80
log β_{pr2}	0.12	Nil

a) In Ref. 1, log K_{dm} was reported to be 2.24.
b) Formation of this species was not concluded within the limit of experimental accuracy.

the two phases were agitated for 30 s. As seen from Fig. 1, the distribution ratio of chromium(III) was dependent on the acid concentration in the acetylacetonate system; in the higher acid concentration range, the distribution ratio was much lower. However, it was not very much affected by the acid in the trifluoroacetylacetonate system although it was a little lower in the highest acid concentration range. It was also found in the both systems in this stage of back-extraction that the distribution ratio was not affected by the β-diketone concentration.

The data in Fig. 1 was analyzed on the basis of Eqs. 3 and 4 by using a least-squars computer program. It was concluded that the data in the acetylacetonate system could be explained by formation of an associate with two protons but those in the trifluoroacetylacetonate system could be explained by formation of an associate with one proton. The values of equilibrium constant in Eqs. 1 and 3 are listed in Table 1. The solid curves in Fig. 1 is calculated by Eq. 4 which is introduced the values of $\beta_{pr(n)}$ in Table 1.

The back-extraction of chromium(III) became much slower after this two-phase distribution equilibrium of the chromium(III) species was established. This slow back-extraction was assumed to be due to that the ligand dissociation from the CrA$_3$ species and its associates with protons in the aqueous phase was slow.

Figures 2a and 2b give examples of the plot of decrease in the chromium(III) concentration in the

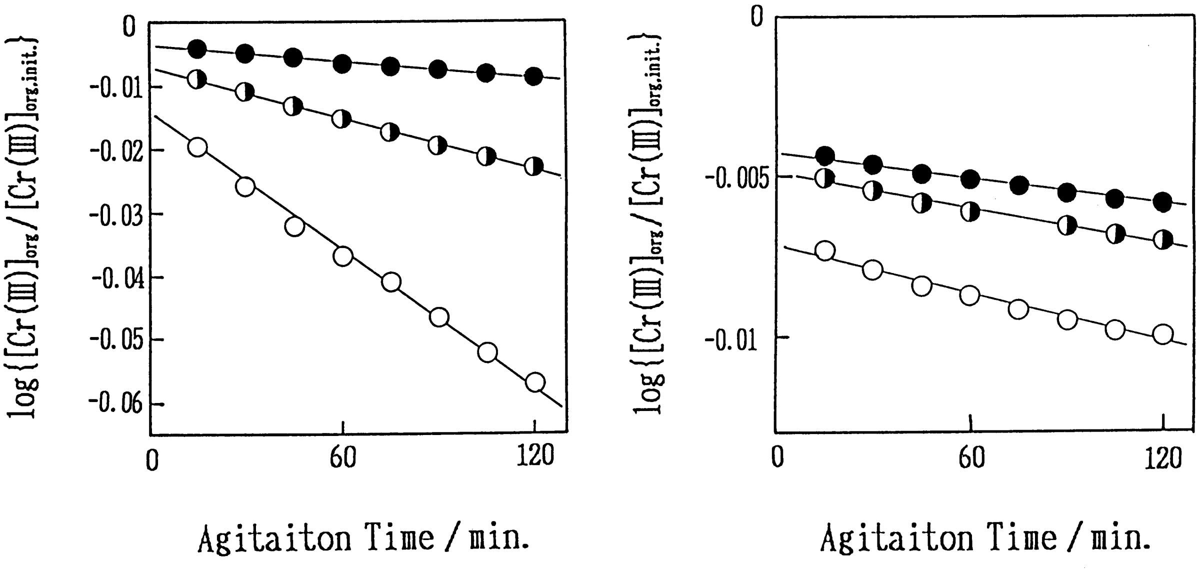

Fig. 2. Decrease in chromium(III) concentration in the organic phase by agitation with aqueous acid perchlorate solutions as a function of agitation time. (a) in acetylacetonate system; hydrogen-ion concentration is 4.0 mol dm^{-3} (○), 3.2 mol dm^{-3} (◑), and 2.5 mol dm^{-3} (●). (b) in trifluoroacetylacetonate system; hydrogen-ion concentration is 4.0 mol·dm^{-3} (○), 2.0 mol·dm^{-3} (◑), and 1.0 mol·dm^{-3} (●).

organic phase as a function of the agitation time (cf. Eq. 7). In both of these figures, the extrapolated values of the plot to the start of two-phase agitation do not agree with zero. This is due to that the rapid back-extraction occurs in the very early stage and the plot in this stage should be much steeper than that given in the figures. From such plots, the dependence of $k_{\mathrm{bex,obsd}}$ on the acid and the β-diketone concentration in the aqueous phase was determined.

Figure 3 gives the dependence of $k_{\mathrm{bex,obsd}}$ on the acid concentration. As seen from Fig. 3, the value of $k_{\mathrm{bex,obsd}}$ in the acetylacetonate system was very much dependent on the acid concentration; the rate of back-extraction was much higher when the acid concentration was higher. However, it is also seen from Fig. 3 that the rate of back extraction in the trifluoroacetylacetonate system was only slightly affected by the acid concentration except in the highest acid concentration range where the rate was a little higher when the acid concentration was higher.

It was also found in the both systems that the rate of back-extraction was not dependent on the β-diketonate ion concentration in the aqueous phase, $[\mathrm{A}^-]$. Thus it can be concluded that the rate-controlling step is the dissociation of the first ligand from the tris-complex and/or its associates with protons in the aqueous phase as is seen from Eqs. 10, 10′, and 10″.

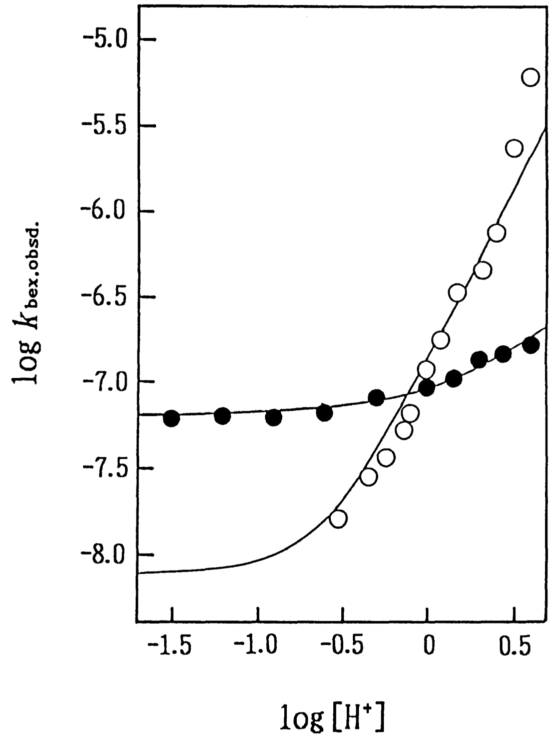

Fig. 3. Dependence of the observed rate constant of back-extraction in acetylacetonate system (open circles) and trifluoroacetylacetonate system (closed circles) on the hydrogen-ion concentration. The solid curves are calculated by Eq. 10 which is introduced the values in Table 2.

Table 2. Rate Constant of the Back-Extraction of $[\mathrm{Cr(acac)_3}]$ and $[\mathrm{Cr(tfa)_3}]$ in Carbon Tetrachloride to Aqueous 4 mol dm^{-3} Perchlorate Solutions (cf. Eq. 6), and of the Aquation of These in Aqueous 4 mol dm^{-3} Perchlorate Solutions (cf. Eq. 10)

	$[\mathrm{Cr(acac)_3}]$	$[\mathrm{Cr(tfa)_3}]$
$\log k_{\mathrm{bex0}}$	−8.1	−7.2
$\log k_{\mathrm{bex1}}$	—	−7.5
$\log k_{\mathrm{bex2}}$	−6.7	—
$\log k_{\mathrm{aq0}}$	−5.0	−5.0
$\log k_{\mathrm{aq1}}$	—	−4.5
$\log k_{\mathrm{aq2}}$	−3.7	—

The dependence of $k_{\mathrm{bex,obsd}}$ of $[\mathrm{Cr(acac)_3}]$ on the acid concentration in Fig. 3 should be explained in terms of the formation of $[\mathrm{Cr(acac)(H^+)_2}]$ species. The data in Fig. 3 were analyzed on the basis of Eq. 10. The slight increase in the $k_{\mathrm{bex,obsd}}$ of $[\mathrm{Cr(tfa)_3}]$ in the highest acid concentration range should be due to a similar reason but the formation of such a species as $[\mathrm{Cr(tfa)_3H^+}]$ was not very clear. The values of $k_{\mathrm{bex}(n)}$ and $k_{\mathrm{aq}(n)}$ for these back-extraction processes are listed in Table 2.

The amount of chromium(III) back-extracted in the acetylacetonate system can be expressed as follows. About 90% of the chromium(III) in the organic phase was back-extracted by two-phase agitation for 48 h when the aqueous phase was 4 mol dm^{-3} perchloric acid but about 14.8, 2.8, 0.7, 0.3, and 0.2% of the chromium(III) in the initial organic phase was back-extracted by the two-phase agitation for 48 h when the aqueous phase contained 2, 1, 0.4, 0.2, and 0.1 mol dm^{-3} perchloric acid, respectively.

The back-extraction in the trifluoroacetylacetonate system proceeded faster than that in the acetylacetonate system in the lower acid concentration range but it proceeded more slowly in the higher acid concentration range because it was only slightly dependent on the acid concentration. Thus, for example, when the aqueous phase was 4 mol dm^{-3} perchloric acid, the amount of back-extracted $[\mathrm{Cr(tfa)_3}]$ into the aqueous phase was estimated to be 2.2% of that in the initial organic phase by a two-phase agitation for 2 hours but it should be 12.4% when the complex was $[\mathrm{Cr(acac)_3}]$, otherwise under identical conditions.

Discussion

The very rapid back-extraction of chromium(III) in the initial stage should be due to the partial transfer of the $\mathrm{CrA_3}$ species from the organic phase to the aqueous phase and a pseudoequilibrium should be established. Since only the $\mathrm{CrA_3}$ species is present in the aqueous phase in the early stage such as after 30 s. two-phase agitation, the distribution ratio, D, of chromium(III) should be approximated to the distribution constant of the $\mathrm{CrA_3}$ species, K_{dm} in Eq. 1 and since this constant may not be very much dependent on the acid concentration, the dependence of D on the acid concentration should be explained in terms of the formation of associates of CrA_3 with protons as described already. Up to now, the reason why only the associate with two protons is formed with the $[Cr(acac)_3]$ species cannot be found. It is marked that the formation of associates with protons is clear with the $[Cr(acac)_3]$ complex but it is not very clear with the $[Cr(tfa)_3]$ complex.

The dependence of rate of back-extraction of the $[Cr(acac)_3]$ species on the hydrogen-ion concentration should be due to that the formation of associates with protons is favorable for rapid back-extraction. This is because (i) it increases the total concentration of the chromium(III) complex in the aqueous phase where the dissociation of the ligand occurs and (ii) the rate of dissociation of ligand from the $[Cr(acac)_3(H^+)_2]$ species is much higher than that from the $[Cr(acac)_3]$ species and the rate of ligand dissociation from the $[Cr(tfa)_3H^+]$ species is somewhat higher than that from the $[Cr(tfa)_3]$ species.

The slow process which appeared after the above rapid back-extraction and continued for a long time should be caused by the dissociation of one or more than one ligands from the complex species in the aqueous phase. This process produced charged species in the aqueous phase which were not extractable into the organic phase. Thus the back-extraction of the most part of chromium(III) from the organic phase should be achieved, even when the complex, CrA_3, would not be changed to its final hydrated Cr^{3+} form.

As it was already described, since no dependence of the rate of back-extraction on the ligand concentration was observed with both the $[Cr(acac)_3]$ and the $[Cr(tfa)_3]$ species, the rate-controlling reaction should not be the dissociation of the CrA_2^+ or CrA^{2+} species in these two systems. This is because if the dissociation of the CrA_2^+ or CrA^{2+} species would be the rate-controlling reaction, the rate should be proportional to $[A^-]^{-1}$ or $[A^-]^{-2}$, as can be seen from Eqs. 10′ and 10″. For this reason, the rate-controlling reaction should be a certain reaction of the CrA_3 species and/or its associates with protons. This could be the dissociation of a ligand from the tris-complex and/or from its associates with protons. Since the acid concentration in the present study was very high, the final form of chromium(III) species in the aqueous phase should be the hydrated Cr^{3+} in the both systems. However, in order to achieve the back-extraction from the organic phase, it is not necessary that the whole chromium(III) species is changed to this final form. If one ligand dissociates from the CrA_3 species, it is enough to cause further back-extraction. This is because the CrA_2^+ species or CrA^{2+} species which can be formed within a much shorter time than the Cr^{3+} species is not extractable. Thus this higher rate of dissociation of the ligand from the CrA_3 or the CrA_2^+ species becomes the controlling rate of the back-extraction. In other words, the back-extraction should proceed much more rapidly than is expected from the rate of "true controlling reaction".

The above results with these chromium(III) β-diketonates are apparently similar to that observed with the rate of back-extraction of tris(benzoylacetonate)-iron(III) ($[Fe(bza)_3]$), in carbon tetrachloride into acid aqueous solutions.[4] In this previous study, the rate of back-extraction was second order dependent on the hydrogen-ion concentration but it was inverse second order dependent on the Hbza concentration. Thus as is indicated by Eq. 10 in the present study, the controlling reaction is assumed to be the dissociation of the last ligand, bza^-, from the $[Fe(bza)]^{2+}$ species. Spectrophotometric measurements in this previous study also supported this assumption. Since the experiments were continued for a relatively shorter period than this previous study, only the rate of dissociation of a ligand from the CrA_3 species and/or its associate with protons was found. These reactions are also slow reactions but still the rate should be much higher than the "true controlling reaction".

In the literature,[5,6] the rate constant for the complex formation of hydrated Cr^{3+} with various ligands is in the range 10^{-5} to 10^{-7} $mol^{-1}\,dm^3\,s^{-1}$. Although not very much is known about the rate constant for the dissociation of ligands from a complex, if the rate constant would also be in this range, it should be reasonable to assume that the value of 1×10^{-5} $mol^{-1}\,dm^3\,s^{-1}$ for the dissociation of the ligand from the CrA_3 in Table 2 should still be higher than the rate constant of the "true controlling reaction".

The associates of $[Cr(acac)_3]$ and $[Cr(tfa)_3]$ with one or two protons which are estimated from the dependence of the distribution ratio of the metal ion on the hydrogen-ion concentration in the early stage of the back-extraction should only be intermediates. These species were recognized because the dissociation of the ligand from the CrA_3 species was slow. Unfortunately, no evidence which shows its structure has been obtained up to now.

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