Rate of Complex Formation and Solvent Extraction of Chromium(III) Produced by the Reduction of Chromium(VI) with Acetylacetone in Aqueous Solutions

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The rate and degree of solvent extraction of chromium(III), which was produced by the reduction of chromium(VI) with ascorbic acid in 0.1 mol dm^{-3} sodium nitrate solutions containing acetic acid/acetate ion as the buffer, were examined by using acetylacetone as the extractant and chloroform as the solvent. The rate of formation of an extractable acetylacetonato complex was greater than that when metal ion was added as hydrated Cr^{3+} until a certain amount of chromium(III) was extracted. Although the rate was first order with respect to the acetylacetone concentration and inverse first order with respect to the hydrogen-ion concentration, the extraction of chromium(III) formed in this way was dependent on the concentration of acetate ions in the aqueous solution. From these results, it was assumed that the chromium(III) produced from chromium(VI) formed a complex with an acetate ion just after the reduction occurred, and that the complex functions as a precursor to the extraction. The acetylacetone reacted with the precursor much more rapidly than the hydrated chromium(III) ion. From the change in the UV-vis spectrum of the complex and in the easiness of stripping of chromium(III) from chloroform with a nitric acid solution, the thus-formed extractable complex was assumed to be an intermediate which changed to a final complex similar to that obtained by the dissolution of crystals of tris(acetylacetonato)chromium(III) in chloroform.

It is known that the solvent extraction of chromium(III) as a non-charged chelate complex into an organic solvent is slow because of the kinetically inert nature of the metal ion. This was found in the solvent extraction of chromium(III) with several β-diketones.[1—7] In the course of a solvent-extraction study of chromium(III) in aqueous solutions containing acetate as the buffer into chloroform with acetylacetone, it was found that the rate of formation of an extractable acetylacetonato complex formed in an aqueous solution when the hydrated chromium(III) ions were formed immediately by reduction of chromium(VI) in the aqueous solution was much greater than that when chromium(III) ions were initially added.[8] The complex thus extracted into chloroform was an intermediate. It gradually changed to the final form while the organic phase was left standing. It was quite similar to the chemical species obtained by the dissolution of tris(acetylacetonato)chromium(III) crystals in the same solvent; it was found from the change in the UV absorption spectrum of the organic phase and also from an observation that the stripping of extracted chromium(III) complex with a nitric acid solution became more difficult while the organic solution containing the metal complex was left standing.[8]

In the present paper, the rate of complex formation of chromium(III) produced by the reduction of chromium(VI) with acetylacetone and the thus-formed solvent extraction of the complex were studied. They were compared with those when the metal ions were added originally in the form of hydrated chromium(III) ions into the aqueous solution.

Experimental

Reagents. All of the reagents were of an analytical grade. The acetylacetone and tris(acetylacetonato)chromium(III) crystals were obtained from Dojindo Laboratories. Potassium dichromate was obtained from Kanto Chemicals, Co. Chromium(III) perchlorate was obtained from Soekawa Chemicals. Co. Sodium nitrate was purified by recrystallization from water. Chloroform was washed by water just before the use.

Procedures. All of the procedures were carried out at 298 K. The complex formation in aqueous solutions or in chloroform and the solvent-extraction experiments were carried out using stoppered glass tubes (capacity 20 cm^3). The vessel was wrapped by an aluminum foil in order to avoid the effect of light. A stock solution of chromium(VI) was prepared by dissolving an amount of potassium dichromate in 1 mol dm^{-3} nitric acid and that of chromium(III) was prepared by dissolving an amount of chromium(III) perchlorate in 1 mol dm^{-3} nitric acid. An aqueous acetylacetone solution was prepared by dissolving a weighed amount of the reagent in a 0.1 mol dm^{-3} sodium nitrate solution and storing overnight. An aqueous 0.1 mol dm^{-3} sodium nitrate solution containing a portion of acetylacetone solution, a weighed amount of ascorbic acid, and an amount of acetate buffer was prepared. To this solution, an amount of 0.1 mol dm^{-3} sodium nitrate solution containing potassium dichromate was added. The initial concentration of chromium was 1.0×10^{-4} mol dm^{-3}. Under the condition of this study, chromium(III) could be produced immediately by the reduction of chromium(VI) in an aqueous solution. The thus-pre-

pared aqueous solution was left standing for a certain given time, and then the same volume of chloroform was added. The two phases were vigorously agitated by a mechanical shaker for 5 min, and were then centrifuged off. Some experiments were also made by using other organic solvents in a similar manner. A portion of the chloroform solution which extracted chromium(III) acetylacetonate was transferred into another tube, and the same volume of 1 mol dm^{-3} nitric acid was added. The two phases were agitated for 30 min in order to strip the extracted chromium(III). This stripping was made just after the extraction, except when it is especially mentioned. The chromium(III) concentration in this stripped solution and that in the aqueous phase of the solvent extraction experiment were determined by atomic-absorption spectrometry. The hydrogen-ion concentration in the aqueous phase was determined by potentiometry using a solution containing 0.01 mol dm^{-3} nitric acid and a 0.09 mol dm^{-3} sodium nitrate solution as the standard of $-\log[H^+] = 2.00$. In the present paper, the thus-obtained value of $-\log[H^+]$ is denoted as pH. For measuring the spectrum, the organic phase was transferred into a quartz cell (one cm light path) and the optical absorption was measured by a spectrophotometer (Hitachi type U-3500) to the reagent blank.

In some experiments, a portion of the chloroform solution which extracted chromium(III) acetylacetonate was placed in glass tubes, which were also covered by aluminum foil and left standing. After the organic solution was left standing for a certain time, and then agitated with 1 mol dm^{-3} nitric acid, the stripped chromium(III) was determined.

Results and Discussion

In the present paper, any chemical species in the organic phase is denoted by the subscript "org" and that in the aqueous phase is denoted by no subscript. The total concentration is denoted by the subscript "tot". The distribution ratio of chromium(III) is defined as $D = [Cr^{III}]_{org.tot}/[Cr^{III}]_{tot.}$

Formation of Extractable Chromium(III) Complex. To an aqueous solution containing acetate buffer and ascorbic acid was added chromium(III) or chromium(VI). For experiments with chromium(III), although no reductant should be necessary, in order to make the conditions similar to those experiments starting with chromium(VI), it was always added. In the present study, the complex formed in the sample aqueous solution at first, and after the solution was left standing, the same volume of the organic solvent was added and the complex was extracted into the organic phase by two-phase agitation.

When acetylacetone was mixed with chromium(III) in aqueous solutions, left standing for a certain given time and then agitated with the same volume of chloroform, the correlation between $\log D$ vs. the standing time is given in Fig. 1 by closed squares. As can be seen from Fig. 1, $\log D$ increases along with the standing time.

It was reported in a previous paper[4] that when the β-diketone was 2-thenoyltrifluoroacetone, the complex extracted into chloroform was not easily stripped, even when the chromium(III) was produced by the reduction of chromium(VI) and stripping was made just after extraction. In this study, when chromium(III) produced by reduction of chromium(VI) with ascorbic acid was extracted as the acetylacetonato complex by agitation with chloroform after the

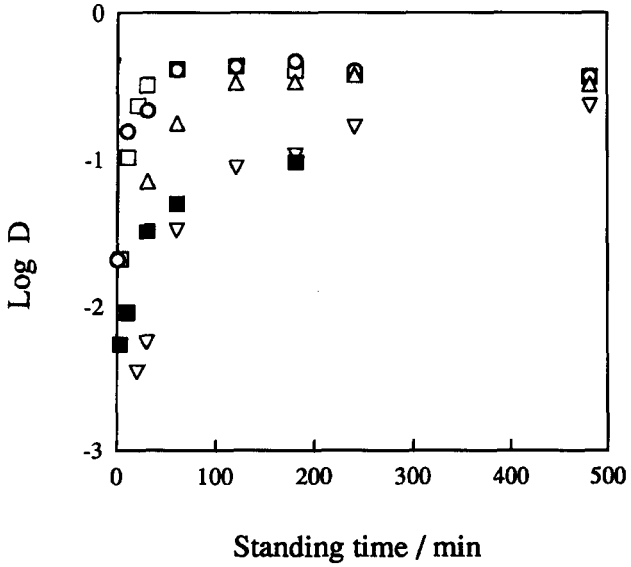

Fig. 1. Change in the extraction of chromium(III) with acetylacetone as a function of the standing time of aqueous solution 0.1 mol dm^{-3} $NaNO_3$ initially containing 0.4 (□), 0.3 (○), 0.1 (△), 0.01 (▽) mol dm^{-3} acetylacetone, 0.01 mol dm^{-3} ascorbic acid, 0.16 mol dm^{-3} acetic acid/acetate ion at pH 5.0 and 1×10^{-4} mol dm^{-3} chromium(VI) (open symbols), or chromium(III) (■). The aqueous phase is left standing for the time given and then it is agitated with the same volume of chloroform.

solution was left standing, the stripping with 1 mol dm^{-3} nitric acid was always quantitative just after the extraction within 30 min. However, it was found that quantitative stripping with 1 mol dm^{-3} nitric acid became more difficult when the chloroform solution extracted chromium(III) with acetylacetone was left standing for a longer time. For this reason, the amount of chromium(III) extracted as an acetylacetone complex was measured by stripping with 1 mol dm^{-3} nitric acid just after the extraction. Figure 1 gives the distribution ratio of chromium(III) produced by the reduction of chromium(VI) as a function of the standing time of the aqueous solution at four different acetylacetone concentrations. As can be seen from Fig. 1, the rate of extraction is greater when the acetylacetone concentration in the aqueous solution is higher. However, it can also be seen from Fig. 1 that the value of distribution ratio obtained after the solution was left standing for a long time (8 h), was not very much different, even when the acetylacetone concentration was different from 0.01 to 0.4 mol dm^{-3}: the value of the distribution ratio reached approximately $10^{-0.40}$ at all of these acetylacetone concentrations. If the extraction equilibrium could be reached, the dominant species in the aqueous phase was Cr^{3+} or its hydrolyzed species, and the extracted species was in the form of $Cr(acac)_3$; also, the distribution ratio, D, at a certain hydrogen-ion concentration should be proportional to the third order of the acetylacetone concentration. For example, when the acetylacetone concentration was 0.4 mol dm^{-3}, the distribution ratio should be $10^{4.8}$-times higher than when the concentration was 0.01 mol dm^{-3}. It was

found that the extraction of the chromium(III) produced by the reduction of chromium(VI) was not affected by the concentration of ascorbic acid over the range from 3×10^{-3} to 3×10^{-1} mol dm^{-3}.

The effect of acetate ions, which were originally added as the buffer, was examined by changing their concentration. A series of aqueous solutions were prepared by changing the free acetate ion concentration, but keeping the hydrogen-ion concentration constant by the addition of a mixed solution of acetic acid and sodium acetate. The acetate ion concentration was calculated using the pK_a value, 4.76. Figure 2 gives the dependence of the distribution ratio on the free acetate ion concentration in the aqueous phase under otherwise identical conditions. It can be seen from Fig. 1 that when the acetylacetone concentration was 0.4 mol dm^{-3}, the maximum extraction in this stage, $D = 10^{-0.4}$, was reached within 1 h. For this reason, the data in Fig. 2 are assumed to give this maximum extraction under the stated conditions. As can be seen from Fig. 2, the value of distribution ratio at this maximum extraction is proportional to the free acetate ion concentration.

In order to examine the effect of acetate ions, the extraction was measured when a solution initially containing a certain concentration of acetate ions and ascorbic acid was added to chromium(VI), and was left standing for different times before the addition of the extractant, acetylacetone. The aqueous solutions contained 0.01 mol dm^{-3} ascorbic acid, 0.16 mol dm^{-3} acetic acid/acetate ion at pH 4.0 and at pH 5.0, to which was added 1×10^{-4} mol dm^{-3} chromium(VI). The sample aqueous solutions were left standing 3, 5, 10, 30, 60, 80, 100, and 120 min and then into each solution was added 0.4 mol dm^{-3} acetylacetone. The solutions were further left standing for 1 h. The distribution ratio when the aqueous solution was agitated with the same volume of chloroform was not affected by the time before the addition of acetylacetone if the solution was left standing for one hour after the addition of acetylacetone. Thus, the distribution ratio was essentially not affected by the standing time of the solution before acetylacetone was added. These results suggest that chromium(III) formed by the reduction of chromium(VI) reacted with the acetate ions within a very short time, and that a 1 : 1 associate of chromium(III) and acetate ion should have been formed. Then, the associate reacted with acetylacetone. In other words, the chromium(III) formed by the reduction of chromium(VI) associated with acetate ion immediately, and the product then reacted with acetylacetone; thus, the 1 : 1 associate of chromium(III) and acetate ion should be a "precursor" to form the extractable acetylacetonato complex. Therefore, the precursor would react with acetylacetone more rapidly than the hydrated chromium(III) ion.

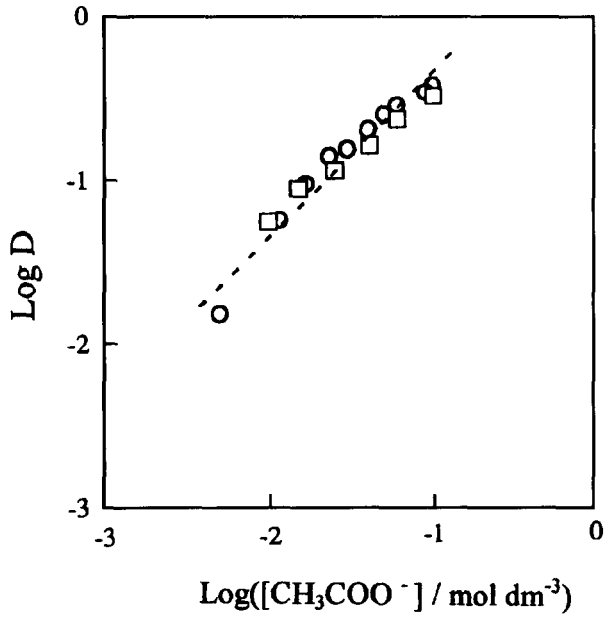

Fig. 2. Dependence of chromium extraction into chloroform on the acetate ion concentration in the aqueous phase. Aq phase: 0.1 mol dm^{-3} $NaNO_3$ initially containing 0.4 mol dm^{-3} acetylacetone, 2.50×10^{-4}—1.35×10^{-3} mol dm^{-3} ascorbic acid, 4.09×10^{-3}—0.46 mol dm^{-3} acetic acid/acetate ion at pH 5.0 (○), pH 4.0 (□) and 1×10^{-4} mol dm^{-3} chromium(VI). The aqueous phase is left standing for the time given and then it is agitated with the same volume of chloroform. The slope of broken line is +1.

It has been examined whether other materials could function as a precursor like the acetate complex or not. To aqueous solutions containing 0.03 mol dm^{-3} or 0.1 mol dm^{-3} acetate, 0.4 mol dm^{-3} acetylacetone, and 0.01 mol dm^{-3} ascorbic acid at pH 5.0, as in the experiments described in Fig. 2, was further added 0.1 mol dm^{-3} of fluoride, chloride, sulfate or trichloroacetate. The solution was left standing for 1 h after the addition of chromium(VI) and agitated with chloroform. It was found that the addition of fluoride ions decreased the distribution ratio from $D = 10^{-0.4}$ to $10^{-1.3}$ (in aqueous solutions containing 0.1 mol dm^{-3} free acetate ion). However, the other three kinds of ions did not affect the extraction; thus, only acetate ions formed the presursor, even in the presence of these ions. Experiments were also made by using 0.1 mol dm^{-3} of propionate and also 0.1 mol dm^{-3} of pyridine as the buffer, but without the addition of acetate ion. It was found that the extraction when propionate was added was quite similar to that when acetate was added. However, when pyridine was added, no such effect, observed with the addition of acetate ion, was found. Thus, such an acceleration of the extraction rate was found only with a propionic acid other than acetic acid. It is reasonable that propionate ions caused a similar effect to that caused by acetate ions, because the difference in the chemical properties of acetate and propionate is rather small. It is assumed that the acceleration due to the carboxylate ions was not due to the carboxylate group, because trichloroacetate did not cause such an acceleration effect. It is reasonable that propionate ions caused a similar effect to that caused by acetate ions, because the difference in the chemical properties of acetate and propionate is rather small. It is assumed that the acceleration produced by the carboxylate ions was not due to the carboxylate group, because trichloroacetate did not cause such an acceleration effect.

The extraction of the extractable chromium(III) complex at this stage was achieved very rapidly. The distribution ratio of chromium(III) at this stage was essentially the same when the two-phase agitation was continued for 1 to 30 min. The formation of an extractable acetylacetonato complex during this two-phase agitation should be slightly formed.

The extraction of chromium(III) in the aqueous phase was, however, not quantitative by agitating with the same volume of chloroform. Under the experimental conditions shown in Fig. 1, the maximum distribution ratio was $10^{-0.4}$; in other words, the extractability was 28.5%. After this first extraction, still some amount of the extractable complex remained in the aqueous phase. When the aqueous solution separated after the first extraction was agitated with the same volume of chloroform, about 8% of the chromium(III) in the first aqueous phase was extracted again. The aqueous phase was then separated from the organic phase, and was agitated with the same volume of chloroform. By this third extraction, about 2% of the chromium(III) present in the first aqueous phase was extracted.

This was further confirmed by a series of back-extraction experiments in a similar manner as mentioned above. Since 1×10^{-4} mol dm^{-3} chromium(VI) was added into an aqueous solution containing 0.4 mol dm^{-3} acetylacetone, 0.16 mol dm^{-3} acetic acid/acetate ion, and 0.01 mol dm^{-3} ascorbic acid at pH 5, the solution was left standing for 2 h. It was then agitated with the same volume of chloroform and separated. This organic phase was transferred into another tube, which was agitated with the same volume of a preequilibrated aqueous solution (which initially contained the reagents at the same concentrations but no chromium, and it had been agitated once with the same volume of chloroform), and the two phases were agitated for 5 min. Then, the amount of chromium(III) back-extracted was determined. After the organic phase was transferred into another tube, the same volume of such a preequilibrated aqueous phase was added and the two phases were agitated. Both phases were then separated and the amount of back-extracted chromium(III) was determined. This back-extraction process was repeated once more. The results are given in Table 1. As can be seen from Table 1, about 21% of the acetylacetonatochromium-(III) complex which had been extracted into the organic phase was back-extracted. Since the dissociation of the acetylacetonate ions from the complex in the aqueous phase should not be very much within such a short time, because of the inertness of chromium(III), the value should be constant for the following transient equilibrium and the value of K^*_{dm} should be $10^{0.6}$ under the conditions written in Table 1:

$$Cr^*(acac)_3 \rightleftarrows Cr^*(acac)_{3\,(org)};$$

$$K^*_{dm} = [Cr^*(acac)_3]_{(org)}\,[Cr^*(acac)_3]^{-1}. \quad (1)$$

Here, $Cr^*(acac)_3$ denotes the intermediate complex. This agrees with the results obtained when the forward extraction was repeated. That is, the proportion of extracted chromium-(III) to the remaining chromium(III) in the aqueous phase decreased by repeating the extraction. This is because about 79% of the extractable complex formed in the aqueous phase was already extracted into the organic phase and about 79% of the remaining extractable complex in the aqueous phase was extracted by the second extraction; that is, about 16.4% of the extractable complex initially formed was extracted by this second extraction. By the third extraction, about 3.7% of the extractable complex initially formed was extracted.

This partial extraction of chromium(III) acetylacetonate from the aqueous phase to chloroform indicates that the chemical properties of the extractable complex in this stage should be different from those of the tris(acetylacetonato)-chromium(III) complex finally found in the organic phase; thus, the extracted complex in this stage should be an intermediate.

It can be seen from the results in Table 2 that when the chloroform solution obtained by the dissolution of tris-(acetylacetonato)chromium(III) crystals was agitated with a preequilibrated aqueous solution, the distribution constant ($K_{dm} = [Cr(acac)_3]_{(org)}\,[Cr(acac)_3]^{-1}$) in the two-phase system was $10^{2.9}$. This value of K_{dm} nearly agrees with the previously reported value.[10]

The extraction of an intermediate from the same aqueous solution into different solvents was measured, and it was found that the extraction was very different among different solvents. The results are also listed in Table 2. The values given in Table 2 indicate that the intermediate acetylacetonatochromium(III) complex should be rather ionic; the best extraction was obtained into chloroform, but the worst ex-

Table 2. Distribution Constant of the Cr(acac)$_3$ Complex between the Two-Phase System

Solvent	log D	log K^*_{dm}	log K_{dm}
$CHCl_3$	−0.4	0.6	2.9
1.2-DCE	−0.8	−0.1	2.5
MIBK	−1.0	−0.4	1.1
Toluene	−1.7	−1.2	2.0
CCl_4	−1.9	−1.4	2.1

Table 1. Back Extraction of Intermediate in Chloroform into Aqueous Solution Which Should Give the Two-Phase Distribution Equilibrium of the Complex
$K^*_{dm} = [Cr^*(acac)_3]_{org}\,[Cr^*(acac)_3]^{-1}$

Run	Chromium remained in the organic phase/mol dm^{-3}	Chromium removed to the aqueous phase/mol dm^{-3}	Amount back extracted/%	log K^*_{dm}
1	2.92×10^{-5}	0.771×10^{-5}	21.0	0.58
2	2.36×10^{-5}	0.592×10^{-5}	20.1	0.60
3	1.79×10^{-5}	0.519×10^{-5}	22.6	0.53

traction was obtained into carbon tetrachloride among these solvents. A similar tendency in the extraction into different organic solvents is often found with the extraction of ion-pairs of cationic metal ions and bulky anions and also with those of anionic metal complexes with bulky cations.

Rate of Formation of Chromium(III) Complex. The rate of formation of an extractable complex of chromium(III) formed from chromium(VI) was dependent on the concentration of acetylacetone and hydrogen-ions, but was not dependent on the acetate concentration, although the acetate was indispensable for quick complex formation. The distribution ratio was measured as a function of the standing time of the aqueous solution.

The rate can be written by the following equation:

$$-\mathrm{d}[\mathrm{Cr^{III}}]/\mathrm{d}t = k[\mathrm{Cr^{III}}][\mathrm{Hacac}]^{a}\,[\mathrm{H^{+}}]^{b}. \quad (2)$$

Equation 2 could be used for the data when the chromium(III) was initially in the form of hydrated chromium(III) ion. As described, only the chromium(III) species with the acetate ions was assumed to react rapidly with acetylacetone. The amount should have been different when the acetate concentration was different, but the concentration was not measured directly. However, it could be calculated under assumptions that (i) the destruction of the precursor was negligible before complex formation; (ii) all of the precursor had an ability to form an extractable acetylacetonato complex. When 0.1 mol dm^{-3} free acetate and 0.4 mol dm^{-3} acetylacetone were present in the solution at pH 5.0 in the presence of 0.01 mol dm^{-3} ascorbic acid, the distribution ratio at the maximum extraction in this stage was always $\log D = -0.4$; that is, 28.5% of the total chromium(III) was extracted. Since, as can be seen from the value of K^{*}_{dm} in Table 1, about 79% of the extractable complex was transferred into chloroform by a single extraction, the percentage of the species could be calculated to be 36% (28.5%/0.79) of the total chromium(III) under these conditions.

Since only the precursor had an ability to form an extractable complex quickly, the rate of the formation of extractable complex after the aqueous solution is left standing by contacting with no organic solvent, could be represented by Eq. 3 using the concentration of the chromium(III) in the precursor form, denoted by $\mathrm{Cr^{III}}$*, for instead of Eq. 2,

$$-\mathrm{d}[\mathrm{Cr^{III*}}]/\mathrm{d}t = k^{*}[\mathrm{Cr^{III*}}][\mathrm{Hacac}]^{a}\,[\mathrm{H^{+}}]^{b}, \quad (3)$$

where k^{*} is the rate constant. This equation can be rewritten as:

$$\log([\mathrm{Cr^{III*}}]/[\mathrm{Cr^{III*}}]_{\mathrm{init}}) = -(k_{\mathrm{obsd}}/2.303)t, \quad (4)$$

$$k_{\mathrm{obsd}} = \mathrm{k^{*}}[\mathrm{Hacac}]^{a}\,[\mathrm{H^{+}}]^{b}. \quad (5)$$

The value of $[\mathrm{Cr^{III*}}]$ is calculated by $[\mathrm{Cr^{III*}}]_{\mathrm{init}} - [\mathrm{Cr^{III}}]_{\mathrm{org}}$ when the volume of the two phases is the same. The distribution ratio was measured as a function of the standing time at nine different acetylacetone concentrations at pH 5.0 and at ten pH values when the acetylacetone concentration was 0.40 mol dm^{-3}. A $\log([\mathrm{Cr^{III*}}]/[\mathrm{Cr^{III*}}]_{\mathrm{init}})$ vs. t plot was made for each series of data of these experiments, and k_{obsd} was obtained from the slope of the plot at an early stage. Figure 3 gives the $\log k_{\mathrm{obsd}}$ vs. log [Hacac] and Fig. 4 gives the $\log k_{\mathrm{obsd}}$ vs. pH. As can be seen from Fig. 3, the rate is first-order dependent on the acetylacetone concentration; from Fig. 4, the rate is inverse first-order dependent on the hydrogen-ion concentration. Thus Eq. 3 can be rewritten as

$$-\mathrm{d}[\mathrm{Cr^{III*}}]/\mathrm{d}t = k^{*}[\mathrm{Cr^{III*}}][\mathrm{Hacac}][\mathrm{H^{+}}]^{-1}. \quad (6)$$

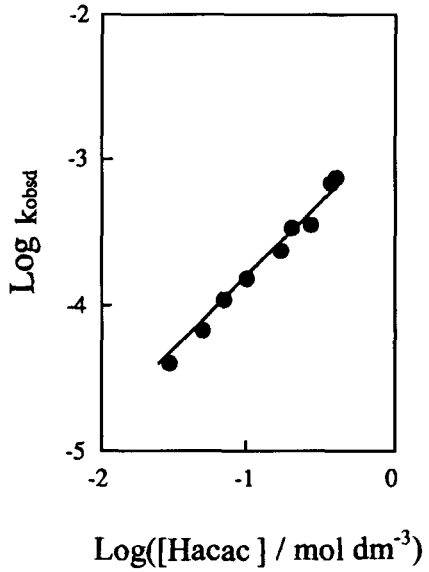

Fig. 3. Dependence of the observed rate constant on Hacac concentration. Aq phase: 0.1 mol dm^{-3} $NaNO_3$ at pH 5.0 containing Hacac, 0.01 mol dm^{-3} ascorbic acid, 0.16 mol dm^{-3} acetic acid/acetate ion, and 1×10^{-4} mol dm^{-3} chromium(VI). The straight line is calculated on the basis of Eq. 5 by introducing k^{*} as $10^{-7.8}$ mol dm^{-3} s^{-1}.

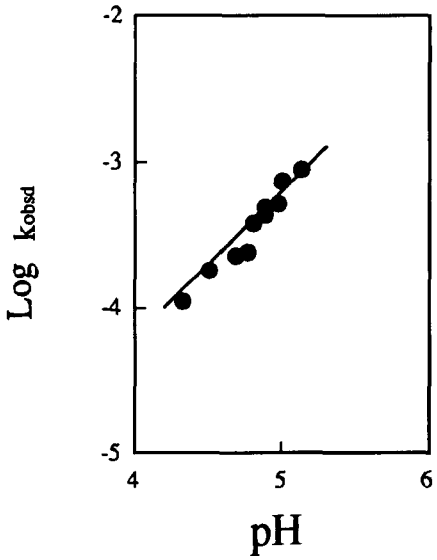

Fig. 4. Dependence of the observed rate constant on the hydrogen-ion concentration. Aq phase: 0.1 mol dm^{-3} $NaNO_3$ containing 0.4 mol dm^{-3} Hacac, 0.01 mol dm^{-3} ascorbic acid, 0.16 mol dm^{-3} acetic acid/acetate ion, and 1×10^{-4} mol dm^{-3} chromium(VI). The straight line is calculated on the basis of Eq. 5 by introducing k^{*} as $10^{-7.8}$ mol dm^{-3} s^{-1}.

The rate constant for the complex formation when the chromium(III) was initially added in the form of hydrated chromium(III) ion, k, was determined from the data given by closed squares in Fig. 1 on the basis of Eq. 2; the value was calculated to be $10^{-8.9}$ mol dm^{-3} s^{-1}, which is similar to that obtained previously.[1] Also, the rate constant for the complex formation of the precursor with acetylacetone was determined from the data in Figs. 3 and 4 on the basis of Eq. 3, k^*, to be $10^{-7.8}$ mol dm^{-3} s^{-1}. Thus, the precursor reacted with acetylacetone 13-times more quickly than did the hydrated chromium(III) ion.

Extracted Species in the Organic Phase. When the chloroform phase into which the chromium(III) complex was extracted was separated just after the two-phase agitation and was left standing, the absorbance in the range of 350 to 450 nm gradually increased and the spectrum became quite similar to that of chloroform solution which was obtained by dissolution of the crystals of tris(acetylacetonato)chromium-(III) as was previously reported (Fig. 2 in Ref. 8).

The change in the complex species from the intermediate to the final one in chloroform was also examined by stripping experiments. The chromium in chloroform extracted the chromium(III) complex produced by the reduction of chromium(VI), was quantitatively stripped by agitation for 5 min with the same volume of 1 mol dm^{-3} nitric acid, just after the extraction. However, when the thus-obtained chloroform solution was left standing, the amount of chromium(III) stripped by agitation with 1 mol dm^{-3} nitric acid gradually decreased, and after 3 days the amount became very small. The change in the amount of chromium(III) stripped in this way as a function of the time that the chloroform solution was left standing is given in Table 3.

It was observed that the extraction was not different even when the sodium nitrate concentration in the aqueous phase changed from 0.01 to 1 mol dm^{-3} as long as the concentrations of acetate and acetylacetone was the same, the pH was the same, and the standing time of the solution was the same (Ref. 8 page 144). This independence of the extraction from the nitrate concentration suggests that the extracted intermediate complex should combine with three acetylacetonate ions, but no nitrate ions. However, it is assumed that the nature of the bond between the metal ion and the ligand ions in the intermediate complex should be different from that in the final complex.

Table 3. Decrease in Cr*(acac)$_3$ Concentration in $CHCl_3$ as a Function of the Standing Time Obtained by the Decrease in the Strippable Chromium(III) by Agitation with 1 mol dm^{-3} HNO_3.

Left standing time/h	$\{[Cr^*(acac)_3]_{org}/[Cr^*(acac)_3]_{org,init}\}$/%
0	100
1	96
4	83
7.5	72
21	42
24	37
29	29
45	17
72	8

The data in Table 3 were treated by the following equation when the concentration of the intermediate complex decreased by its change to the final complex:

$$-d[Cr^*(acac)_3]_{org}/dt = k_t[Cr^*(acac)_3]_{org}[Hacac]^a_{org}, \quad (7)$$

where k_t is the rate constant for the transformation of the complex. This equation can be rewritten as

$$\ln([Cr^*(acac)_3]_{org}/[Cr^*(acac)_3]_{org,init}) = -k_t[Hacac]^a_{org} \times t. \quad (8)$$

The observed rate constant for this transformation of the complex from the intermediate to the final may be written as

$$k_{obsd} = k_t[Hacac]^a_{org} = -\log([Cr^*(acac)_3]_{org}/[Cr^*(acac)_3]_{org,init}) \times 2.303/t. \quad (9)$$

Eq. 8 can be written as

$$\log([Cr^*(acac)_3]_{org}/[Cr^*(acac)_3]_{org,init}) = -(k_{obsd}/2.303) \times t. \quad (10)$$

Figure 5 gives a plot calculated from the data in Table 3 on the basis of Eq. 10. From Fig. 5, the observed rate constant, k_{obsd}, was observed to be $10^{-4.7}$ under the given conditions.

It was found that the rate of change of the intermediate to the final complex was not affected by the concentration of the coexisting acetylacetone in chloroform. This was found both in the absorption spectrum and in the amount of the chromium(III) to be stripped by 1 mol dm^{-3} nitric acid. Thus, the value of "a" in Eq. 7 should be zero. While the

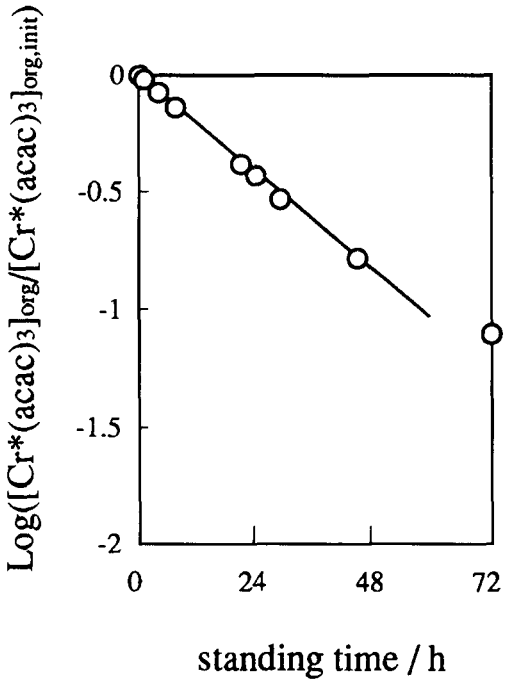

Fig. 5. Rate of back-extraction of extracted complex in chloroform as a function of the standing time of chloroform solution with 1 mol dm^{-3} HNO_3. The data are listed in Table 3.

organic phase is left standing, the intermediate complex is transformed to the final complex. It is reasonable that the rate of this transformation from the intermediate to the final one is similar to that of the formation of various complex from the hydrated Cr^{3+} ions in aqueous solutions with several ligands, such as benzoyltrifluoroacetone (Hbfa), benzoylacetone (Hbza), trifluoroacetylacetone (Htfa),[3] 2-thenoyltrifluoroacetone (Htta)[4] in a previous study. This is because the bonds between the central metal ion and the acetylacetonate ions in the intermediate complex should be rather ionic and that in the final complex they should form coordination bonds. They should be rearranged during the transformation from ionic bonds to coordination bonds.

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