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Rate of Solvent Extraction of Chromium(III) with Acetylacetone into Carbon Tetrachloride

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The rate of solvent extraction of chromium(III) in aqueous perchlorate solutions into carbon tetrachloride as the tris(acetylacetonato) complex has been determined. The rate was first order with respect to the acetylacetone concentration and inverse first order with respect to the hydrogen-ion concentration. From this information, the rate-controlling reaction is concluded to be the formation of the first complex in the aqueous phase by a reaction between $[Cr(OH)]^{2+}$ and HA.

Since the rate of solvent extraction of chromium(III) in aqueous solutions with chelating extractants is very low, this experimental method can be used only when it is enhanced, for example, by heating the aqueous solutions containing hydrated Cr^{3+} ions in the presence of the extractant[1)] or by the complex formation of metal ions with a second ligand, such as fluoride ions.[2)]

In the course of a series of kinetic studies on the solvent extraction of chromium(III) with β-diketones, it has been found that the rate of extraction with acetylacetone (2,4-pentanedione, HA) was much higher when the diluent was 4-methyl-2-pentanone (MIBK) than when it was carbon tetrachloride; the extraction into the latter solvent was negligible, even after two-phase agitation for 24 h, while it was measurable into the former solvent under identical conditions, except for the diluent.[3)]

In the present study, the rate of extraction of Cr^{3+} in aqueous sodium perchlorate solutions into this nonpolar solvent with β-diketone was measured at a much higher ligand concentration than in the previous work and the mechanism of the extraction process as well as the rate-controlling reaction was considered.

Experimental

All the experiments were carried out at 298 K. The solvent and reagents were of reagent grade. The tris(acetylacetonato)chromium(III) was obtained from Dojindo Laboratories. Sodium perchlorate was recrystallized three times from water. Carbon tetrachloride was washed twice with water before use. The aqueous solutions were 4 mol dm^{-3} sodium perchlorate constant ionic media containing 1×10^{-3} mol dm^{-3} of Cr^{3+} and 5×10^{-3} mol dm^{-3} of sulfanilic acid-sulfanilate buffer which kept the hydrogen-ion concentration from 10^{-3} to $10^{-4.5}$ mol dm^{-3}. Experiments were carried as follows: A portion of the aqueous solution and the same volume of an organic solution of acetylacetone was placed in a stoppered glass vessel. The two phases were agitated at such a speed that no increase in the rate was found upon further increasing the agitation speed for a certain time; they were then centrifuged. The content of the tris(acetylacetonato)chromium(III), CrA_3, in the organic phase was determined from the optical density at 380 nm and the chromium(III) concentration in the aqueous phase was determined by an atomic absorption method.

The distribution constant of the CrA_3 complex was determined as follows. A carbon tetrachloride solution containing 1×10^{-3} mol dm^{-3} of the complex and 1×10^{-1} mol dm^{-3} of acetylacetone was agitated with the same volume of an aqueous perchlorate solution for 3 min; then the two phases were centrifuged off. The chromium(III) content in the aqueous phase was determined by the atomic absorption method.

Results and Discussion

In the present paper, all species in the organic phase are denoted by "org" and that in the aqueous phase by using no subscript. The volumes of the two phases were the same. The hydrogen-ion concentration was always higher than 1×10^{-5} mol dm^{-3}. The pK_a of the reagent was about 10.1[4)] and was in large excess to the metal ions. Under these conditions, the following equation may be written for the extractant in the aqueous phase:

$$[HA]_{total}=[HA]+[A^-]+\sum a[CrA_a^{3-a}]. \qquad (1)$$

The value of distribution constant of the CrA_3 complex, $K_{dm}=[CrA_3]_{org}/[CrA_3]$, was obtained to be $10^{2.24}$.

It was found that the rate of solvent extraction was not affected by the speed of the two-phase agitation. There was no difference in the rate of solvent extraction when the two phases in the vessel were continuously agitated using a mechanical shaker and when they were agitated by hand for a few minutes after they were left standing in the dark after an initial agitation of the two phases. Furthermore, when an aqueous solution which contained the metal ions, acetylacetone, and the buffer was left standing in the dark for a certain time and agitated with a carbon tetrachloride solution of acetylacetone for 30 min, the amount extracted was similar to that when the two phases were continuously agitated. These results indicate that the rate controlling reaction is the complex formation in the aqueous phase and that it is neither a reaction on the interface nor in the organic phase.

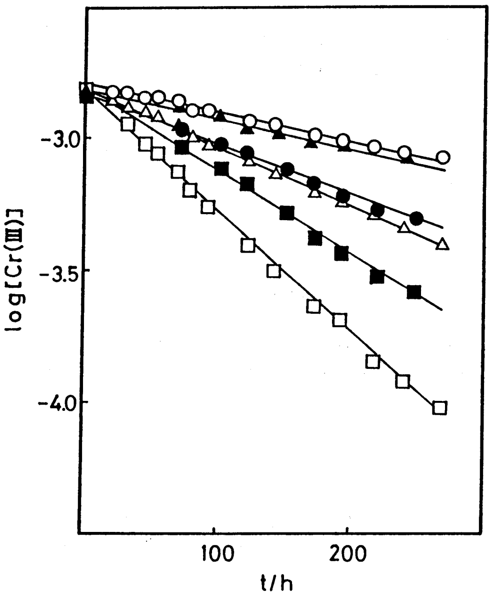

Fig. 1. Amount of extracted Cr(III) as tris(acetylacetonato) complex into carbon tetrachloride as a function of standing time of the system. The pH of solution is; 3.42 (○), 3.93 (△), 4.46 (□), 3.89 (●), 3.45 (▲), and 4.32 (■).

Figure 1 shows the decrease in the chromium(III) concentration in the aqueous phase upon solvent extraction as a function of time. As can be seen from Fig. 1, each set of data can be represented by a straight line and, thus, the rate of extraction should be first order with respect to the total chromium(III) concentration in the aqueous phase. The rate of solvent extraction, V_{se}, can be given by the decrease in the chromium(III) concentration in the aqueous phase, [Cr(III)], and can be written

$$\begin{aligned} V_{se} &= -d[\mathrm{Cr(III)}]/dt \\ &= k_{obsd}[\mathrm{Cr(III)}]. \end{aligned} \quad (2)$$

Figure 2 gives a log k_{obsd} vs. log [HA] plot for a $-\log[H^+]$ of 3.6. As can be seen from Fig. 2, the values of k_{obsd} are first order with respect to [HA] and, thus, the formation of the first complex should be the rate-determining step.

Figure 3 gives the dependence of k_{obsd} on the hydrogen-ion concentration. In this figure, the value of $k_{obsd}/[HA]$ is given on the basis of the results in Fig. 2 in order to compare the data at different extractant concentrations. The plot in Fig. 3 is not a straight line but a curve. After trials, the following equation was found to fit well with the experimental data when $C_1=10^{-8.9}$ and $C_2=10^{-4.3}$:

$$\log(k_{obsd}/[HA])=\log(C_1/(C_2+[H^+])). \quad (3)$$

The above values of C_1 and C_2 are introduced into Eq. 3. The broken line in Fig. 3 is calculated by using this data. Thus, Eq. 2 can be rewritten as

$$V_{se}=C_1[\mathrm{Cr(III)}][HA]/([H^+]+C_2). \quad (4)$$

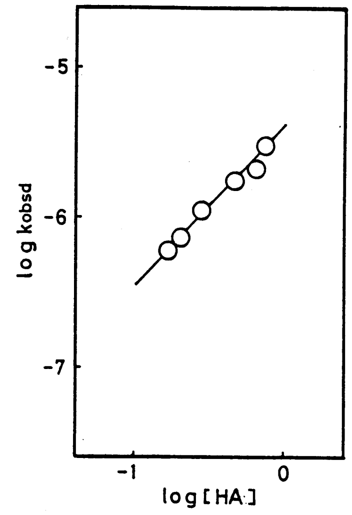

Fig. 2. Rate of complex formation as a function of concentration of acetylacetone in undissociated form in aqueous phase. The slope of the line is +1.

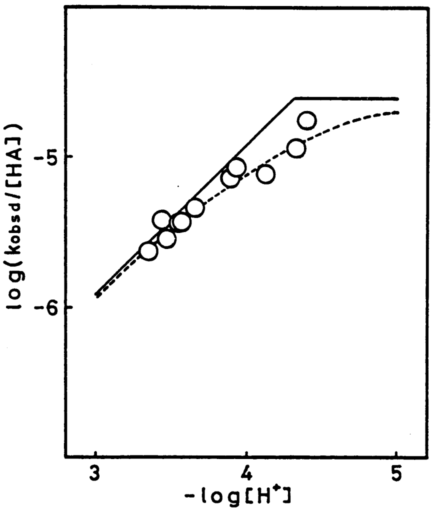

Fig. 3. Rate of solvent extraction of Cr(III) into carbon tetrachloride as a function of hydrogen ion concentration. Aqueous phase: 4 mol dm^{-3} $NaClO_4$. The broken line is the calculated curve by using Eq. 3 with $C_1=10^{-8.9}$ and $C_2=10^{-4.3}$. Each asymptote give the value when $[H^+]\to\infty$ and $[H^+]\to 0$.

When the rate-controlling reaction is the formation of the first complex in the aqueous phase, it can be given by one or both of the following equations:

$$[\mathrm{Cr(OH)}]^{2+}+HA \quad (5)$$

and/or

$$Cr^{3+}+A^-. \quad (6)$$

The rate of complex formation, V_{cf}, may be given by

$$V_{cf}=k_1[\mathrm{Cr(OH)}^{2+}][HA]+k_2[Cr^{3+}][A^-]. \quad (7)$$

When only the following hydrolysis is taken into the account,

$$[\mathrm{Cr(H_2O)_6}]^{3+}\rightleftarrows[\mathrm{Cr(OH)(H_2O)_5}]^{2+}+H^+$$

and

$$K_h=[\mathrm{Cr(OH)}^{2+}][\mathrm{H}^+]/[\mathrm{Cr}^{3+}], \tag{8}$$

the total amount of uncomplexed chromium(III) can be given as

$$\begin{aligned}[\mathrm{Cr(III)}]_{\mathrm{uncomp}} &= [\mathrm{Cr}^{3+}]+[\mathrm{Cr(OH)}^{2+}] \\ &= [\mathrm{Cr}^{3+}](1+K_h/[\mathrm{H}^+]). \end{aligned} \tag{9}$$

The formation of polymerized species such as $[\mathrm{Cr_2(OH)_2}]^{4+}$, $[\mathrm{Cr_2(OH)_3}]^{3+}$, and $[\mathrm{Cr_2(OH)_4}]^{2+}$ by the hydrolysis of chromium(III) has been pointed out.5) For example, when $-\log\,[\mathrm{H}^+]$ is 4 and the total chromium(III) concentration is 1×10^{-3} mol dm^{-3}, the formation of polymerized species after 10 days can be calculated by using the constants;5) this value was found to be about 10%. Thus, effects due to the polymerized species could be neglected in the considerations of the rate in the early stage of the reaction. By using Eq. 8, Eq. 7 can be written as

$$V_{\mathrm{cf}}=(k_1K_h+k_2K_a)[\mathrm{Cr}^{3+}][\mathrm{HA}]/[\mathrm{H}^+], \tag{10}$$

where K_a is the acid dissociation constant, $K_a=[\mathrm{H}^+][\mathrm{A}^-]/[\mathrm{HA}]$, and K_h is the hydrolysis constant in Eq. 8. The value of the constant in the literature is4) $K_a=10^{-10.1}$. The value of K_h in the literature ranges6) from $10^{-3.5}$ to $10^{-4.2}$; a value of $10^{-4.3}$ was reported in a recent paper.5)

On the basis of Eq. 9, Eq. 10 can be rewritten as

$$V_{\mathrm{cf}}=(k_1K_h+k_2K_a)[\mathrm{Cr(III)}]_{\mathrm{uncomp}}\,[\mathrm{HA}]/([\mathrm{H}^+]+K_h). \tag{11}$$

When $[\mathrm{Cr(III)}]_{\mathrm{uncomp}}$ is almost the same as [Cr(III)], it should be regarded from Eqs. 4 and 11 that $C_1=(k_1K_h+k_2K_a)$ and $C_2=K_h$.

In this data analysis, it was assumed that $[\mathrm{Cr(III)}]_{\mathrm{uncomp}}$ is equal to [Cr(III)]; that is, the total concentration of the acetylacetonato complex species, $[\mathrm{CrA}^{2+}]+[\mathrm{CrA_2}^+]+[\mathrm{CrA_3}]$, is negligible compared to $[\mathrm{Cr(III)}]_{\mathrm{uncomp}}$. Separate experiments were made in order to examine this as follows. A portion of the aqueous phase was separated from the organic phase after two-phase agitation for a certain time. This was again agitated for a certain time with the same volume of carbon tetrachloride containing the same concentration of the extractant, but with no chromium(III). It was found that no chromium(III) in the aqueous phase was extracted by this second extraction. When the $[\mathrm{CrA}]^{2+}$ and/or $[\mathrm{CrA_2}]^+$ species are present in appreciable amounts in this separated aqueous phase, each should react with the ligand at a higher rate than of the rate-controlling reaction to form the $\mathrm{CrA_3}$ species, which is extracted well as the K_{dm} value indicates. For this reason, the amounts of these species and of the $\mathrm{CrA_3}$ species is, for all practical purposes, negligible compared to the amount of Cr^{3+} or $[\mathrm{Cr(OH)}]^{2+}$ in this aqueous solution.

Due to a proton ambiguity, it is generally impossible to conclude whether Eq. 5 or 6 is the rate-controlling reaction. However, the former seems to control the whole process; if the former was the controlling reaction, the value of k_1K_h would be calculated to be $10^{-8.9}$ (s^{-1}) and, consequently, the value of k_1 would be obtained as $10^{-4.6}$ (mol^{-1} dm^3 s^{-1}). The keto-enol equilibrium of the β-diketone should be taken into account. Since the enol form of acetylacetone is only 20% of the undissociated form,7) ($K_e=[\mathrm{HA}]_{\mathrm{enol}}/[\mathrm{HA}]_{\mathrm{keto}}=10^{-0.63}$), the rate constant should be about 5-times higher if only the enol form of the β-diketone reacts in the way given by Eq. 5. However, it still is seen that the rate constant, k_1, is about 10^{-4} (mol^{-1} dm^3 s^{-1}). If the latter would control the extraction, the value of k_2K_a should be equal to $10^{-8.9}$ (s^{-1}). As pointed out, K_a in these ionic media is $10^{-10.1}$ (mol dm^{-3}) and, consequently, k_2 is calculated to be $10^{1.2}$ (mol^{-1} dm^3 s^{-1}).

In the literature,8,9) 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}), while that of $[\mathrm{Cr(OH)}]^{2+}$ is in a range 10^{-3} to 10^{-5} (mol^{-1} dm^3 s^{-1}). The present results, $k_1\simeq10^{-4}$ (mol^{-1} dm^3 s^{-1}), suggest that the complex formation in the system studied proceeds through a reaction of the $[\mathrm{Cr(OH)}]^{2+}$ species with the undissociated form of acetylacetone, HA.

The mechanism of water exchange of hydrated Cr^{3+} and $[\mathrm{Cr(OH)}]^{2+}$ was considered from the viewpoint of the activation volume of the reaction.8) It was concluded that the water exchange from the Cr^{3+} species proceeded through an $\mathrm{I_a}$ mechanism while the reaction for that from the $[\mathrm{Cr(OH)}]^{2+}$ species had a dissociative character. The difference of the rate constant for the complex formation of the hydrated Cr^{3+} and $[\mathrm{Cr(OH)}]^{2+}$ species may possibly be explained by the difference in the reaction mechanism. However, the conclusion does not seem to be definite.

The ratio of the total amount of the complexes formed in the system and the amount extracted is given as

$$\begin{aligned}R &= [\mathrm{CrA_3}]_{\mathrm{org}}/([\mathrm{CrA}^{2+}]+[\mathrm{CrA_2}^+]+[\mathrm{CrA_3}]+[\mathrm{CrA_3}]_{\mathrm{org}}) \\ &= K_{\mathrm{dm}}\beta_3[\mathrm{A}^-]^3/(\beta_1[\mathrm{A}^-]+\beta_2[\mathrm{A}^-]^2 \\ &\qquad +\beta_3[\mathrm{A}^-]^3+K_{\mathrm{dm}}\beta_3[\mathrm{A}^-]^3),\end{aligned} \tag{12}$$

where β_n is the stability constant of the "n-th" complex. Since the value of K_{dm} is $10^{2.24}$, it can be concluded that nearly all of the complexes formed are extracted as the $\mathrm{CrA_3}$ species into the organic phase when this ratio is approximately unity; however, if R is to some extent smaller than unity, the complexed chromium(III) which remains in the aqueous phase cannot be neglected.10)

It was reported that the rate constant for the complex formation with the same ligand obtained by the data of solvent extraction into MIBK is several orders higher than the present value.4) This problem will be considered in another paper.

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