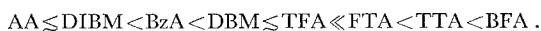


Synergistic Effect in Solvent Extraction of Scandium β -Diketone TOPO System

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The terminal group effect of β -diketones on the synergism was studied in scandium- β -diketone-TOPO system. Eight β -diketones, acetylacetone (AA), diisobutyrylmethane (DIBM), benzoylacetone (BzA), dibenzoylmethane (DBM), trifluoroacetylacetone (TAA), benzoyl-trifluoroacetone (BFA), thenoyltrifluoroacetone (TTA) and froyltrifluoroacetone (FTA) were employed as the chelating agent. The scandium β -diketonates reacted with trioctylphosphine oxide (TOPO) to form the ScR_3L type adduct, and the stability constant of the adducts increased in the following order:



The tendency may be attributed to the strong electron withdrawal of a trifluoromethyl group and the resonance effect of a phenyl group, which increase the residual coordination power of the metal ion. The steric effect of the terminal group on the synergism was not recognizable.

I. INTRODUCTION

It has been well known as synergistic effect that the presence of neutral ligands, such as organophosphorus compounds, enhances the extraction of metal β -diketonates. This phenomenon results from the adduct formation of metal β -diketonates with neutral ligands, and the synergistic effect has been widely investigated from the various points of view in many metal- β -diketone-neutral ligand systems¹⁾⁻⁴⁾.

In the present research, the effect of the terminal groups of β -diketone on the synergism was studied in scandium- β -diketone-TOPO system. The study on this effect has been carried out only in zinc⁵⁾, uranyl⁶⁾ and lutetium⁷⁾ β -diketonate system. In this investigation, scandium was chosen as a metal ion for comparing with rare earth metals. Scandium ion has a comparatively smaller ionic radius, although it shows similar chemical property to rare earth ions which give striking synergism. Therefore, it is very interesting to compare the terminal group effect on the adduct formation of scandium chelates and of rare earth chelates, especially from a standpoint of the steric hindrance.

The extraction constant of scandium chelates and the stability constant of the adducts were obtained by using β -diketones, such as acetylacetone (AA), diisobutyrylmethane (DIBM), benzoylacetone (BzA), dibenzoylmethane (DBM), trifluoroacetylacetone (TAA), benzoyltrifluoroacetone (BFA), thenoyltrifluoroacetone (TTA) and froyltrifluoroacetone (FTA). These β -diketones, which were shown in Table I, were classified into three groups; β -diketones containing methyl group, phenyl group and trifluoromethyl group, respectively.

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Table I. β -Diketones.

β -diketone	R ₁	R ₂
Acetylacetone (AA)	CH ₃	CH ₃
Diisobutyrylmethane (DIBM)	(CH ₃) ₂ CH	(CH ₃) ₂ CH
Benzoylacetone (BzA)	C ₆ H ₅	CH ₃
Dibenzoylmethane (DBM)	C ₆ H ₅	C ₆ H ₅
Trifluoroacetylacetone (TAA)	CF ₃	CH ₃
Benzoyltrifluoroacetone (BFA)	C ₆ H ₅	CF ₃
Thenoyltrifluoroacetone (TTA)		CF ₃
Froyltrifluoroacetone (FTA)		CF ₃

II. EXPERIMENTAL

Apparatus.

Radioactivity measurements were carried out with a NaI well-type scintillation counter (44.5 mm in dia. $\times$ 50.8 mm), equipped with a Metro digital scaler, model MP-6A. A Hitachi-Horiba pH meter, model M-4, was used for the pH measurements.

Materials.

Scandium-46 was obtained from New England Nuclear Corp. as chloride in hydrochloric acid solution, and the solution was fumed with perchloric acid to make the perchlorate solution. All the reagent grade β -diketones were supplied from Dojindo Co. Ltd. and trioctylphosphine oxide (TOPO) was purchased from Tokyo Kasei Kogyo Co. Ltd. Except AA and TAA which were purified by distillation, these β -diketones and all other materials were used without further purification.

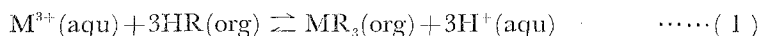
Procedure.

The procedure was almost the same as described in the previous papers³⁾⁵⁾. Five milliliters of aqueous solution containing ⁴⁶Sc³⁺ tracer, sodium perchlorate (0.1 M) and acetic acid (0.01 M) are controlled to a desired pH, transferred into a glass stoppered tube and shaken with the same volume of benzene solution containing β -diketone and TOPO, at about 25°C. After centrifugalous separation of two layers, 2 ml of each phase were pipetted out into test tubes and the gamma-activities were counted with the scintillation counter. The pH values of aqueous phase were measured again and were used for plotting the data. The distribution ratio of scandium was given by the following equation:

$$D = \frac{\gamma\text{-count rate per 2 ml of organic phase}}{\gamma\text{-count rate per 2 ml of aqueous phase}}$$

III. THEORETICAL

In the extraction of tervalent metal ion with β -diketone, HR, the extraction equilibrium and the extraction constant, K_e , can be expressed as follows;



$$K_e = \frac{[\text{MR}_3]_{\text{org}} [\text{H}^+]_{\text{aqu}}^3}{[\text{M}^{3+}]_{\text{aqu}} [\text{HR}]_{\text{org}}^3} \quad \dots\dots (2)$$

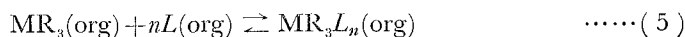
where the suffixes “org” and “aqu” denote the species in the organic and the aqueous phase, respectively. If the intermediate complexes, such as MR^{2+} and MR_2^+ , are negligible, the distribution constant is given by the equations:

$$D = \frac{[\text{MR}_3]_{\text{org}}}{[\text{M}^{3+}]_{\text{aqu}}} = K_e \frac{[\text{HR}]_{\text{org}}^3}{[\text{H}^+]_{\text{aqu}}^3} \quad \dots\dots (3)$$

or

$$\log D = \log K_e + 3 \log [\text{HR}]_{\text{org}} + 3 \text{ pH} \quad \dots\dots (4)$$

When a neutral ligand, L , present in the organic phase reacts with metal β -diketonate to form the adduct as



$$\beta_n = \frac{[\text{MR}_3L_n]_{\text{org}}}{[\text{MR}_3]_{\text{org}} [L]_{\text{org}}^n} \quad \dots\dots (6)$$

the distribution ratio, D^* , is now obtained from the equation,

$$\begin{aligned} D^* &= \frac{[\text{MR}_3]_{\text{org}} + \sum_{n=1}^n [\text{MR}_3L_n]}{[\text{M}^{3+}]_{\text{aqu}}} \\ &= K_e \frac{[\text{HR}]_{\text{org}}^3}{[\text{H}^+]_{\text{aqu}}^3} \left(1 + \sum_{n=1}^n \beta_n [L]^n \right) \quad \dots\dots (7) \end{aligned}$$

From Eqs. (3) and (7), the next equation is introduced at a definite pH;

$$D^*/D = 1 + \sum_{n=1}^n \beta_n [L]^n \quad \dots\dots (8)$$

and when the MR_3L type adduct is predominant, the stability constant, β_1 , can be easily obtained from the following equation:

$$D^*/D = 1 + \beta_1 [L] \quad \dots\dots (9)$$

or

$$\log (D^*/D - 1) = \log \beta_1 + \log [L] \quad \dots\dots (10)$$

IV. RESULTS AND DISCUSSION

Scandium- β -diketone System.

The distribution data are shown in Figs. 1, 2 and 3, as the $\log D$ vs. pH plots, which were obtained in the absence of TOPO. From the Eq. (4), it is expected that the plots should be a straight line with a slope of three under the constant concentration of β -diketone. But the slope obtained deviates downwards from the theoretical value. This fact may be caused by the formation of water-soluble complexes, such as ScR^{2+} , ScR_2^+ etc., or by the formation of hydroxo-complexes. Sekine and his co-workers reported the presence of water-soluble complexes and obtained the formation

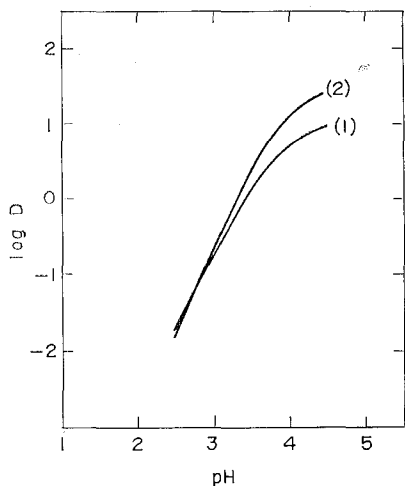


Fig. 1. Distribution of scandium as a function of pH.

(1) 0.1 *M* AA (2) 0.1 *M* DIBM

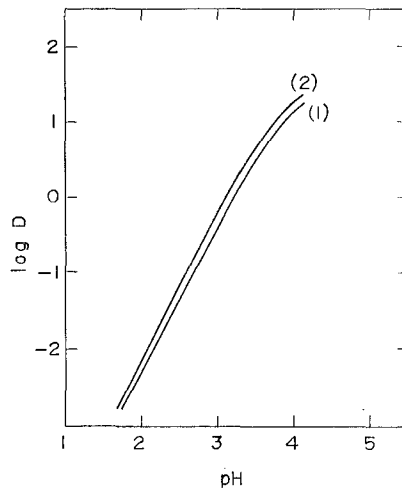


Fig. 2. Distribution of scandium as a function of pH.

(1) 0.05 *M* BzA (2) 0.05 *M* DBM

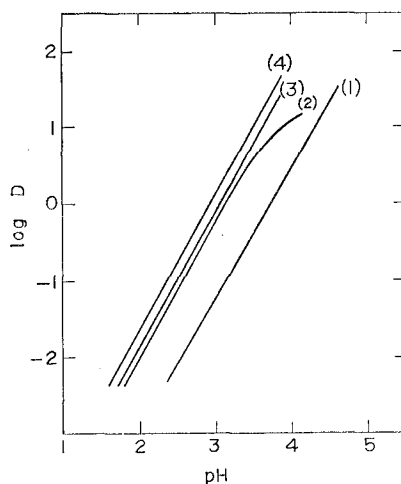


Fig. 3. Distribution of scandium as a function of pH.

(1) 0.002 *M* BFA (2) 0.01 *M* TAA
(3) 0.002 *M* TTA (4) 0.002 *M* FTA

constants in scandium AA and scandium TTA systems⁸⁾. In the present research, however, the detailed experiment was not performed, since the formation of these complexes may not essentially affect on the calculation of the stability constant of the adducts.

In Table II, the extraction constants of scandium β -diketonates are summarized, with the acid dissociation constants of the β -diketones. The values of the extraction constants should not be taken as very exact ones, but as only measures of the extractability, because the extractions have not been done ideally as described above. The extractability increases in the following order:

Synergistic Effect in Scandium β -Diketone TOPO System

Table 2. Extraction constant of scandium β -diketone chelates and stability constant of the adducts.

β -diketone	pK_a^*	$\log K_e$	$\log \beta_1$
Acetylacetone	12.75	-6.15	4.20
Diisobutylmethane	—	-6.15	4.40
Benzoylacetone	12.85	-4.95	4.65
Dibenzoylmethane	13.75	-4.80	5.05
Trifluoroacetylacetone	8.70	-1.20	5.10
Benzoyltrifluoroacetone	9.20	-1.40	6.30
Thenoyltrifluoroacetone	9.10	-0.35	5.70
Froyltrifluoroacetone	8.50	-0.25	5.50

* Negative logarithm of the acid dissociation constant of the β -diketone in 75 vol. % dioxane.
[L. G. van Uitert, W. C. Fernelius and B. E. Douglas, *J. Am. Chem. Soc.*, **75**, 457 (1953)].

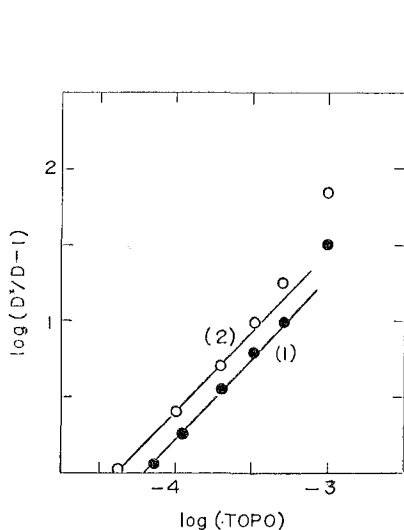


Fig. 4. The plot of $\log(D^*/D-1)$ against $\log[TOPO]$.
(1) AA (2) DIBM

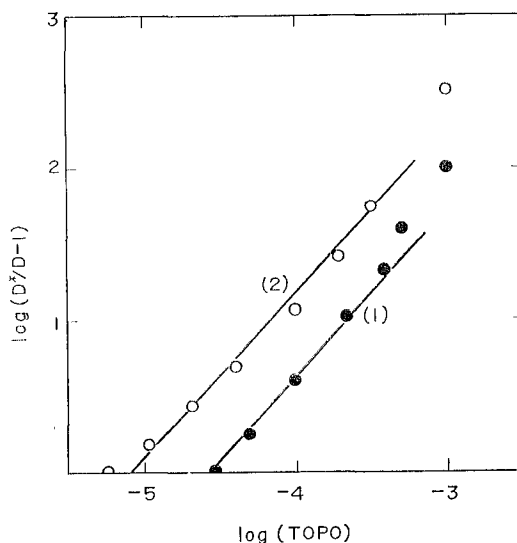


Fig. 5. The plot of $\log(D^*/D-1)$ against $\log[TOPO]$.
(1) BzA (2) DBM

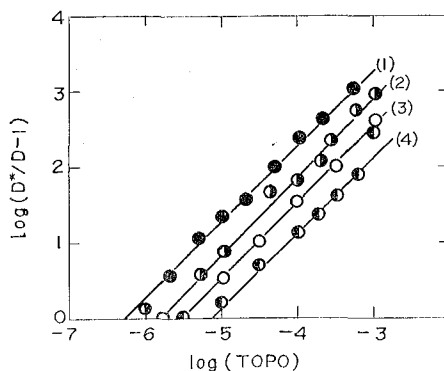


Fig. 6. The plot of $\log(D^*/D-1)$ against $\log[TOPO]$.
(1) BFA (2) TTA (3) FTA (4) TAA



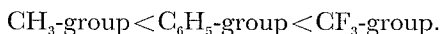
The result agrees with the previous observations and the tendency was explained in detail⁹⁾.

Scandium- β -diketone-TOPO System.

The D^* values were measured by varying the TOPO concentration at a constant concentration of β -diketone, and the $\log(D^*/D-1)$ values were plotted against $\log [\text{TOPO}]$. Straight lines with a slope of 1, in Figs. 4, 5 and 6, indicate that one mole of the scandium chelate reacts with one mole of TOPO to form the ScR_3L type adduct in the TOPO concentration range studied. The values of $\log \beta_1$ were graphically obtained and were presented in Table II. The stability of the adduct rises in the following order of β -diketone:



In general, the synergistic effect increases in the following sequence:



This tendency is the same with those in uranyl, zinc and lutetium- β -diketone-TOPO systems, and was previously discussed⁵⁾⁻⁷⁾. Namely, a trifluoromethyl group strongly withdraws electrons from the surroundings of the coordination bond between central metal ion and the β -diketone, and a phenyl group gives the resonance effect to π -electron of the chelate ring. Accordingly, the substitution of a methyl group with such groups should weaken the interaction between the metal ion and the ligand and must increase the residual coordination power of the metal ion, and such a situation may be favorable for the adduct formation.

As indicated in Table II, the stability constant of scandium-BzA-TOPO adduct is much lower than that of the DBM-TOPO adduct. This fact suggests that the steric effect of the terminal group of β -diketones was not an important factor on the synergism, even in such a small central metal ion as scandium ion (0.68 Å).

REFERENCES

- (1) D. Dyrssen and L. G. Sillen, *Acta. Chem. Scand.*, **7**, 663 (1953).
- (2) D. Dyrssen and L. Kuca, *Acta. Chem. Scand.*, **14**, 1945 (1960).
- (3) T. Shigematsu, M. Tabushi, M. Matsui and T. Honjyo, *Bull. Chem. Soc. Japan*, **40**, 2807 (1967).
- (4) T. V. Healy, D. F. Peppard and G. W. Mason, *J. Inorg. Nucl. Chem.*, **24**, 1429 (1962).
- (5) T. Shigematsu, M. Tabushi, M. Matsui and K. Utsunomiya; *This Bulletin*, **45**, 290 (1967).
- (6) K. Batzar, D. E. Goldberg and L. Newman; *J. Inorg. Nucl. Chem.*, **29**, 1511 (1967).
- (7) T. Honjyo, *Bull. Chem. Soc. Japan*, in press.
- (8) T. Sekine, A. Koizumi and M. Sakairi, *ibid.*, **39**, 2681 (1966).
- (9) T. Sekine, M. Sakairi, F. Shimada and Y. Hasegawa, *ibid.*, **38**, 2087 (1965).