

The Synergistic Effect in the Solvent Extraction of Europium and Zinc Benzoyltrifluoroacetate Adducts with Phosphine and Arsine Oxides

Tôru AOKI, Etsuo DEGUCHI, Masakazu MATSUI and Tsunenobu SHIGEMATSU

Received August 3, 1971

The influence of organic Lewis base on the solvent extraction of europium and zinc benzoyltrifluoroacetates was studied. Triphenylarsine oxide (TPAsO), triphenylphosphine oxide (TPPO), tri-*n*-octylphosphine oxide (TOPO), methylenebis-(diphenylphosphine oxide) (MBDPO) and ethylenebis (diphenylphosphine oxide) (EBDPO) were employed for the neutral ligand. Reacting with europium chelate, dioxide ligands form the adducts of MR_3L type, but monooxide ligands make the adducts of MR_3L_2 type. The stability constant of the monooxide adducts increases in the following order: TPPO < TPAsO $\approx$ TOPO. The influence of the neutral ligand on the synergistic effect in the zinc chelate system increases in the following sequence: TPPO < EBDPO < MBDPO < TOPO.

INTRODUCTION

Some metal chelates can often be extracted at a lower pH region by adding neutral Lewis bases to the extraction system. Such phenomena called "synergistic effect" was at first reported by Cuninghame, *et al.*¹⁾ Since this report, the synergistic enhancement of metal chelate extraction has been found in various systems and the theoretical considerations of the reactions have also been reported by many investigators.²⁾ The enhanced extraction observed was attributed to the adduct formation between metal chelate and neutral ligand.

In our previous papers, the synergistic research was carried out on the adduct formation of metal β -diketonates with some neutral ligands.³⁻⁵⁾ Especially the effect of the central metal ion and the relationship between the ionic radius of the metal and the stability constant of the adduct were investigated.

The adduct-forming reaction suggests that metal β -diketone chelates may be used as a standard for estimating the basicity of neutral ligands. The present work reports the adduct formation of divalent zinc and trivalent europium benzoyltrifluoroacetate chelates with triphenylarsine oxide and with phosphine monooxides and dioxides. From the adduct formation, the basicity of these neutral ligands are also examined.

EXPERIMENTAL

Apparatus and Reagents—Radioactivity countings were made with a TEN NaI(Tl) (44.5 mm in dia. $\times$ 50.8 mm) well-type scintillation counter, Model EA-14,

* 青木 達, 出口日雄, 松井正和, 重松恒信: Laboratory of Radiochemistry, Institute for Chemical Research, Kyoto University, Uji, Kyoto.

connected with a Metro dekatron scaler, Model MCL-6B. A Hitachi-Horiba glass electrode pH meter, Model M-5, was used for the pH measurements.

The europium 152+154 and zinc 65 tracers were obtained from the Oak Ridge National Laboratory as hydrochloric acid solutions, and were diluted to make solutions of about 1 μ Ci/ml.

Methylenebis (diphenylphosphine oxide), MBDPO, was synthesized by the oxidation of methylenebis (diphenylphosphine) with hydrogen peroxide in acetone solution. Methylenebis (diphenylphosphine) was prepared by the reaction of dichloromethane with sodium diphenylphosphide in liquid ammonia.⁶⁾ The ditertiary phosphine was recrystallized from propane-1-ol, m.p. 121°C (Found: C, 78.4; H, 5.8. Calc.: C, 78.1; H, 5.8%). The dioxide purified from benzene had m.p. 187°C (Found: C, 72.3; H, 5.4. Calc.: C, 72.1; H, 5.3%). Ethylenebis (diphenylphosphine oxide), EBDPO, was also prepared similarly by use of 1,2-dichloroethane in place of dichloromethane. The compound had m.p. 274°C (Found: C, 72.4; H, 5.6. Calc.: C, 72.5; H, 5.6%).

Triphenylarsine oxide, TPAsO, and triphenylphosphine oxide, TPPO, were prepared by oxidizing triphenylarsine and triphenylphosphine respectively with hydrogen peroxide in acetone solution. Triphenylarsine was synthesized by the reaction of arsenic trichloride with chlorobenzene in the presence of powdered sodium.⁷⁾ Benzoyltrifluoroacetone and tri-*n*-octylphosphine oxide, TOPO, were purchased from the Dojindo Co., Ltd., Research Laboratories. Sodium perchlorate was prepared from sodium hydroxide and recrystallized two times. All other reagents of the reagent grade materials were used without further purification.

Procedure—The procedure of the solvent extraction was essentially the same as that described in previous papers.³⁾ Ten milliliters of an aqueous solution containing radioactive tracer, sodium perchlorate (0.1 M) and acetic acid (0.01 M) were placed in a 30 ml glass-stoppered centrifuge tube. After the pH of the solution was adjusted at a desirable value, 10 ml of benzene containing benzoyltrifluoroacetone (0.05 M) and various amounts of neutral ligand were added.

Two phases in the tube were shaken for 30 minutes and centrifuged until they got clear. Two milliliters of each phase were pipetted out into test tubes, and the γ -activities were measured with a NaI(Tl) scintillation counter. The pH value of the aqueous phase was checked after the extraction process.

Theoretical treatments in the present work is the same as the previous reports.^{3,5)} The stability constants of the metal chelate adducts, β_n , can be calculated from the following equations:



$$K = [MR_x]_0 \cdot [H^+]^x \cdot [M^{x+}]^{-1} \cdot [HR]_0^{-x} \quad (2)$$



$$K' = [MR_x \cdot L_n]_0 [H^+]^x [M^{x+}]^{-1} [HR]_0^{-x} [L]_0^{-n} \quad (4)$$

$$[MR_x]_0 + n[L]_0 = [MR_x \cdot L_n]_0 \quad (5)$$

$$\beta_n = [MR_x L_n]_0 [MR_x]_0^{-1} [L]_0^{-n} \quad (6)$$

$$D_0 = [MR_x]_0 / [M^{x+}] \quad (7)$$

$$D = ([MR_x]_0 + [MR_x L]_0 + [MR_x L_2]_0 + \dots) / [M^{x+}] \quad (8)$$

$$\begin{aligned} D/D_0 &= 1 + \beta_1[L]_0 + \beta_2[L]_0^2 + \dots \\ &= 1 + \sum \beta_n[L]_0^n \end{aligned} \quad (9)$$

$$\log D/D_0 = \log (1 + \sum \beta_n[L]_0^n) \quad (10)$$

where D_0 and D are the distribution ratio in the absence and in the presence of neutral ligand; M^{x+} stands for x -valent metal ion, HR for benzoyltrifluoroacetone and L for neutral ligand, and $[]$ and $[]_0$ denote the concentration of the chemical species in the aqueous and organic phases, respectively.

RESULTS AND DISCUSSION

Adduct Formation in Europium Benzoyltrifluoroacetate System—

The effect of MBDPO on the extraction of europium with benzoyltrifluoroacetone is shown in Fig. 1. The plots of $\log D/D_0$ vs. $\log [L]_0$ can be obtained from these data. Figure 2 presents the change in the distribution ratio of europium as a function of the concentration of such neutral ligands as MBDPO, EBDPO, TOPO, and TPAsO. The stability constants of these adducts, $\log \beta_n$, are listed in the first and second column of Table 1. As shown in Fig. 2, straight lines with a slope of 1 are obtained when the europium benzoyltrifluoroacetate reacts with diphosphine dioxides, while the maximum slopes become 2 when the europium chelate reacts with monooxides

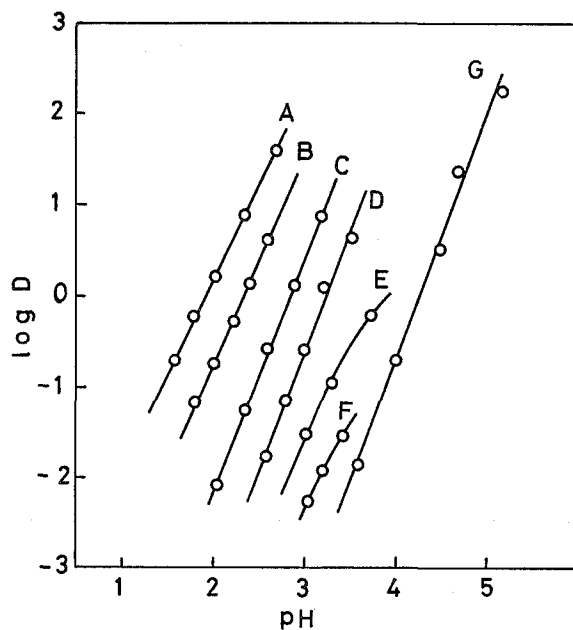


Fig. 1. The distribution ratio of europium with benzoyltrifluoroacetone in the presence of various MBDPO concentrations as a function of pH.

A: $2.5 \times 10^{-4}M$, B: $5.0 \times 10^{-5}M$, C: $5.0 \times 10^{-6}M$,
D: $5.0 \times 10^{-7}M$, E: $5.0 \times 10^{-8}M$, F: $5.0 \times 10^{-9}M$,
G: none.

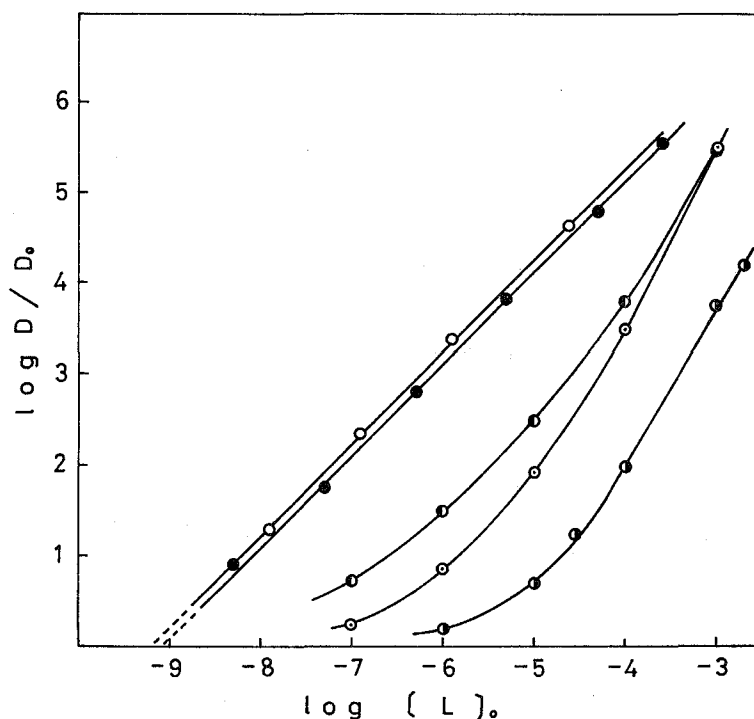


Fig. 2. The variation of the distribution ratio as a function of the neutral ligand concentration in europium chelate system.

○: EBDPO, ●: MBDOPO, ◐: TPAsO,
 ⊙: TOPO, ⊖: TPPO.

such as TOPO, TPPO and TPAsO. It was reported that one mole of europium benzoyltrifluoroacetate reacted with two moles of neutral ligand to form MR_3L_2 -type adduct in benzene.³⁾ Figure 2 also shows the formation of the adducts with two moles of TOPO, TPPO and TPAsO, but the figure indicates that one molecule of MBDOPO and EBDPO binds to one molecule of the europium chelate.

The stability constants of MBDOPO and EBDPO adducts were estimated to be $\log \beta_1=9.10$ and 9.20 , respectively. These values are rather larger than $\log \beta_1$ values

Table 1. Stability Constants of Europium and Zinc Benzoyltrifluoroacetate Adducts with Various Neutral Ligands.

neutral ligand	Eu		Zn
	$\log \beta_1$	$\log \beta_2$	$\log \beta$
TPPO	5.75	9.80	5.20
TPAsO	7.45	11.50	
TOPO	6.85	11.70	6.40
MBDOPO	9.10		6.00
EBDOPO	9.20		5.70

of phosphine monooxide adducts and correspond roughly to $\log \beta_2$ value of TPPO adduct. The stability constant of lutetium adduct with TOPO, where the formation of secondary adducts was not observed, was very similar to $\log \beta_1$ value of the other rare earth adducts with TOPO.³⁾ These facts suggest that diphosphine dioxides may bond to the europium benzoyltrifluoroacetone chelate rather as a bidentate ligand than as a monodentate ligand.

It is supposed that the europium benzoyltrifluoroacetate forms the adduct of six-membered ring with MBDPO, but the chelate makes the adduct of seven-membered ring with EBDPO: There is no significant difference in stability constant between MBDPO and EBDPO adducts.

As mentioned above, such monooxide ligands as TPPO, TOPO and TPAsO react with the europium chelate to form the adduct of MR_3L_2 -type. The overall stability constant of the adduct increases in the following order: TPPO < TPAsO $\approx$ TOPO. The order of TPPO and TOPO reveals that the introduction of the aromatic group into the neutral ligand has a tendency to weaken the basicity of the neutral ligand. This may be partly attributed to the resonance effect or the interaction of π -electron of aromatic group with that of phosphine oxide double bond. The steric effect may not play an important part in lowering the stability, because the ratio of the first stability constant to the second one in TPPO adduct is almost equal to the ratio in TOPO adduct.

Dipole moment of the monooxide ligand increases by the replacement of phos-

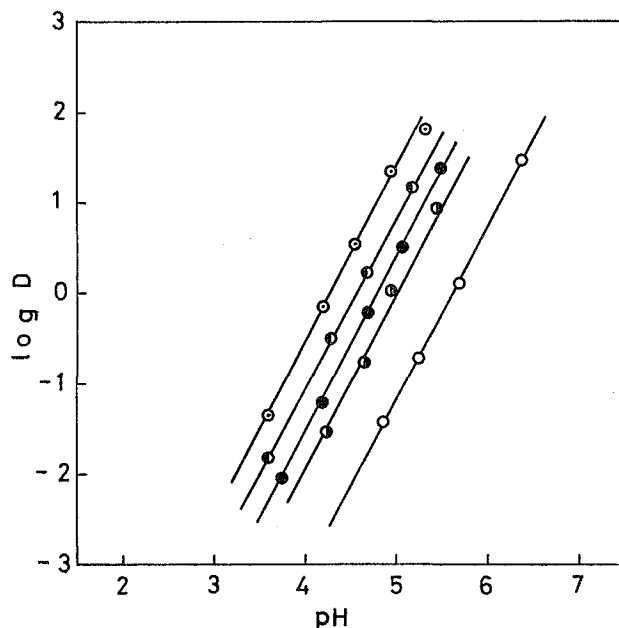


Fig. 3. The distribution ratio of zinc with benzoyltrifluoroacetone in the presence of $1.0 \times 10^{-4}M$ neutral ligand as a function of pH.

○: TOPO, ◐: MBDPO, ●: EBDPO,
◐: TPPO, ○: none

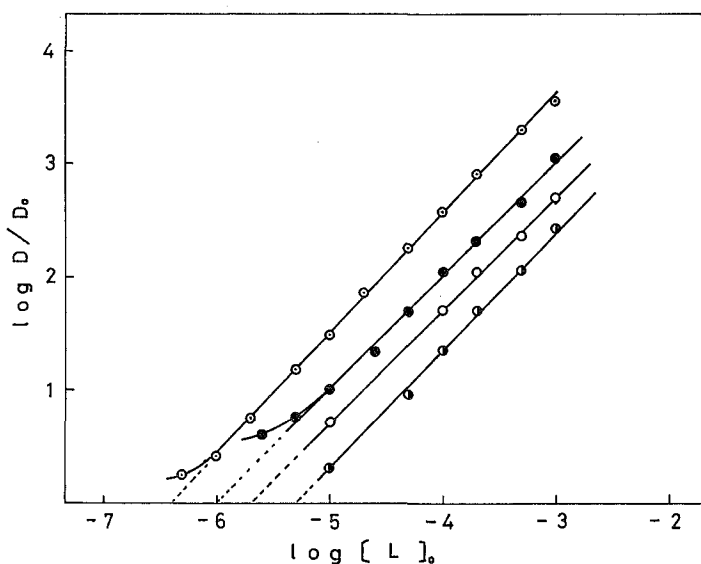


Fig. 4. The variation of the distribution ratio as a function of the neutral ligand concentration in zinc chelate system.

⊙: TOPO, ●: MBDPO, ○: EBDPO, ⊖: TPPO.

phine atom to arsine. This brings the stronger basicity of the ligand. The stability of TPAsO adduct enhanced by the effect becomes equal to that of TOPO adduct. The ratio between the first and the second stability constants shows 0.71 in TOPO, 0.54 in TPAsO and 0.70 in TPPO system. The drop of the ratio in TPAsO system may be caused by steric factor.

Adduct Formation in Zinc Benzoyltrifluoroacetate System—Figure 3 indicates the $\log D$ vs. pH plots in the synergistic extraction of zinc with benzoyltrifluoroacetone and various neutral ligands in benzene. The extraction of zinc is also much enhanced by the adduct formation in the presence of several phosphine oxides. The plots of $\log D/D_0$ vs. $\log [L]_0$ in Fig. 4 shows the effect of various neutral ligands on the adduct formation. The stability constant of the adducts, $\log \beta_1$, can be obtained from the plots and the results are summarized in Table 1. Each asymptote of the plots has a straight line with a slope of 1, which indicates the adduct formation of MR_2L -type. The stability constant of the adducts increases in the following order; TPPO < EBDPO < MBDPO < TOPO.

The higher stability of the TOPO adduct as compared with TPPO system was also observed in zinc chelate system. Diphosphine dioxides would behave as a bidentate ligand in the europium chelates as mentioned above, but bond to the zinc chelate as a monodentate ligand in the present system.

The basicity of the diphosphine dioxides when they behave as a monodentate ligand, is rather stronger than that of TPPO, but weaker than that of TOPO. The MBDPO adduct of the zinc chelate is slightly more stable than the EBDPO adduct. This may be caused by the stronger interaction of phosphine oxide groups.

REFERENCES

- (1) J. G. Cuninghame, P. Scargill and H. H. Willis, Report AERE-C/M-215 (1954).
- (2) T. Honjo and T. Shigematsu, *Kagaku* (Kyoto), **23**, 708 (1968).
- (3) T. Shigematsu, M. Tabushi, M. Matsui and T. Honjo, *Bull. Chem. Soc. Japan*, **39**, 165 (1966); *ibid.*, **40**, 2807 (1967); *ibid.*, **42**, 976 (1969).
- (4) T. Shigematsu, M. Tabushi, M. Matsui and K. Utsunomiya, *Bull. Inst. Chem. Res., Kyoto Univ.*, **45**, 290 (1967)
- (5) T. Shigematsu and T. Honjo, *ibid.*, **47**, 613 (1969).
- (6) W. Hewertson and H. R. Watson, *J. Chem. Soc.*, 1490, 1962.
- (7) R. L. Shriner and C. N. Worf, *Org. Syntheses Col. Vol. IV*, 910 (1963).