

## Synergism in extraction of cobalt in presence of benzoyltrifluoroacetone and various donors

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Received 10 October 1988; accepted 10 July 1989

Synergism in the extraction of cobalt in the presence of a mixture of benzoyltrifluoroacetone and various donors (both O and N donors) has been studied. The nature of adducts formed has been investigated by slope analysis and the equilibrium constants have been evaluated. Synergism increases in the order: sulfoxides < alkyl phosphate < nitrogen donors and shows a correlation with the basicity of the donor.

In studies on synergism in the extraction of metals, various aspects like the nature of chelating agent, donor, diluent etc., have been investigated. Transition metal ions are characterised by variable oxidation states and coordination number. Since synergism may also arise due to an increase in the coordination number of the metal ion, it was thought of interest to study the extraction of a divalent transitional metal ion, viz. cobalt in the presence of benzoyltrifluoroacetone (HBFA) and various donors. The results are reported in this paper.

### Materials and Methods

Cobalt in the form of  $^{60}\text{Co}$  was obtained from Isotope Group, BARC, Bombay. Benzoyltrifluoroacetone (K and K Labs, USA) was used as a solution in toluene (Sarabhai M Chemicals, GR). The donors used were tributyl phosphate (TBP) (BDH, England), triphenylphosphine oxide (TPPO), quinoline (Q) (both from Koch-Light Lab, USA), ethylhexylphosphate (EHP) (K and K Labs), dimethylpyridine (Hopkins and Williams, UK), antipyrine (Magenta Chemicals, Bombay) and trioctylmonomethylammonium chloride (ICN Pharmaceutical, USA), and were used as received.

Extraction experiments were carried out by equilibrating the aqueous phase (10 ml) containing  $\sim 10^{-6}$  M cobalt, sodium perchlorate to maintain the ionic strength at 1.0, acetic acid ( $\sim 0.02$  M) and sodium hydroxide with an equal volume of the organic phase containing the  $\beta$ -diketone and a donor for 3 hr at  $30 \pm 2^\circ\text{C}$ . The two phases were separated and the pH of the aqueous phase was measured using a Beckman Expandomatic SS-2

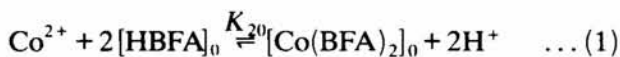
pH meter. Cobalt in the two phases was estimated by measuring the activity of 1.0 ml of the solution by gamma-ray spectrometry using a thallium activated sodium iodide crystal in a single channel analyser. Corrections were made for the background activity.

### Results and Discussion

Synergism in the extraction of cobalt, studied using HBFA and various alkyl phosphates, sulfoxide and nitrogen donors, was observed in all the cases and the extraction due to donors alone was negligible.

#### HBFA system

Extraction of cobalt in toluene was studied using HBFA alone. The distribution ratio was measured as a function of pH at fixed HBFA concentration of 0.025 M as well as at varying concentrations of HBFA at constant pH of 5.40. The  $[\text{HBFA}]_0$  was calculated taking into account the partition coefficient of HBFA<sup>1</sup>. The plots of log D versus log  $[\text{HBFA}]_0$  and pH were linear with slopes of 2.0 and 1.8, respectively, indicating the extraction of  $\text{Co}(\text{BFA})_2$ . The extraction equilibrium can be expressed by Eq. (1)



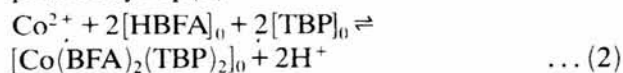
with the equilibrium constant,  $K_{20} = 7.4 \times 10^{-9}$ .

#### HBFA-TBP system

The distribution ratio for the above system was measured as a function of pH at fixed  $[\text{HBFA}]_0$  and  $[\text{TBP}]_0$  as well as at varying  $[\text{HBFA}]_0$  and  $[\text{TBP}]_0$  keeping the pH and concentration of the

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other extractant constant. The plots of log D versus pH, log [HBFA]<sub>0</sub> and log[TBP]<sub>0</sub> were linear having slopes of 1.9, 1.9 and 1.8, respectively indicating the formation of a diadduct, [Co(BFA)<sub>2</sub>(TBP)<sub>2</sub>]. The extraction mechanism can be expressed by Eq. (2).



and the equilibrium constant was calculated as  $3.2 \times 10^{-4}$ .

#### HBFA-EHP system

In the extraction of cobalt as above in the presence of a mixture of HBFA and ethylhexyl phosphate (EHP), the plots of log D versus pH, log[HBFA]<sub>0</sub> and log[EHP]<sub>0</sub> were linear with slopes of 2.0, 2.0 and 1.2, respectively. The equilibrium constant for the formation of the monoadduct, [Co(BFA)<sub>2</sub>EHP] was calculated as  $1.1 \times 10^{-5}$ .

#### HBFA-TPPO system

In this system the pH of 50% extraction was about 5.45 in the presence of a mixture of 0.01 M each of HBFA and TPPO. The plots of log D versus pH and log [HBFA]<sub>0</sub> were linear with slopes of 2.0 while the slope of the plot of log D versus [TPPO]<sub>0</sub> was about 1.3 indicating the presence of both mono and diadducts. The nature of the extracted species was evaluated from the data on the variation of [TPPO].

The distribution ratio, D, can be written as

$$D = \frac{[\text{CoA}_2]_0 + [\text{CoA}_2(\text{TPPO})]_0 + [\text{CoA}_2(\text{TPPO})_2]_0}{[\text{Co}]} \quad \dots (3)$$

assuming cobalt to be present in the aqueous phase mainly as uncomplexed metal ion. The concentration of the anion (A) of HBFA, can be calculated from the pH of the solution and pK value (6.01) of HBFA<sup>1</sup> as well as the partition coefficient ( $10^{2.47}$ ) of HBFA in toluene. The above equation can be written in terms of the equilibrium constants as

$$F_0 = \frac{D[\text{H}]^2}{[\text{HA}]_0^2} = K_{20} + K_{21}[\text{TPPO}]_0 + K_{22}[\text{TPPO}]_0^2 \quad \dots (4)$$

where  $K_{21}$  and  $K_{22}$  refer to the equilibrium constants for the formation of monoadduct and diadduct. The function  $F_0$  was calculated from the distribution ratio measured at different [TPPO]<sub>0</sub> and was solved for the individual constants by the graphical method. The plot of  $F_0$  versus [TPPO]<sub>0</sub> re-

sulted in a curve passing through the origin indicating extraction due to Co(BFA)<sub>2</sub> alone to be negligible. The plot of  $F_1$  versus [TPPO]<sub>0</sub> was linear with the intercept as  $2.5 \times 10^{-5}$  corresponding to  $K_{21}$  and  $1.7 \times 10^{-3}$  as the slope corresponding to  $K_{22}$ . TPPO being a stronger donor forms both mono- and di-adducts.

#### HBFA-DPSO system

In this system the extraction was 50% at a pH of about 5.85 in the presence of 0.01 M HBFA and 0.025 M DPSO, indicating weaker donor strength of DPSO. Analysis of the data indicated the formation of a monoadduct with equilibrium constant as  $6.3 \times 10^{-7}$ .

#### HBFA-AP<sub>y</sub> system

Synergism in the extraction of cobalt using a mixture of HBFA and phenazone or antipyrine (AP<sub>y</sub>) indicated formation of a monoadduct with an equilibrium constant of  $1.0 \times 10^{-5}$ . The concentration of AP<sub>y</sub> in the organic phase was calculated taking into account the partition coefficient of AP<sub>y</sub> as 0.19 which was determined in a separate series of experiments.

#### Synergism in the presence of nitrogen donors:

##### (i) HBFA-Q system

In the case of this system, the plots of log D versus pH and log[HBFA]<sub>0</sub> were linear with slopes of 2.1 and 2.0, respectively. The concentration of quinoline in the organic phase was calculated from Eq. (5)

$$[\text{Q}]_0 = \frac{[\text{Q}]_{\text{tot}} \times 15.85}{P_{\text{HA}} + 1 + \text{H}/K_a} \quad \dots (5)$$

where the partition coefficient<sup>2</sup>  $P_{\text{HA}} = 15.85$  and  $K_a$ , the protonation constant<sup>3</sup>  $= 1.07 \times 10^{-5}$ . The plot of log D[H]<sup>2</sup> versus log[Q]<sub>0</sub> was linear with a slope of 1.8 indicating the existence of the diadduct as the predominant species. The equilibrium constant for the reaction was calculated as  $7.9 \times 10^{-2}$ . Increased synergism could also be inferred from the pH of 50% extraction of 4.1 in the presence of 0.01 M HBFA and 0.05 M Q.

##### (ii) HBFA-DMP system

Extraction of cobalt in the presence of a mixture of HBFA and dimethylpyridine (DMP) was also studied. The plots of log D versus pH and log[HA]<sub>0</sub> were linear with slopes of 3.0 and 2.0 respectively. The plot of log D versus log[DMP]<sub>total</sub> was also linear with a higher slope. This could be attributed to the variation in pH and [DMP] in

the organic phase. The [DMP] in the organic phase was calculated as in the case of quinoline taking into account the partition coefficient<sup>2</sup> as 20.5 and protonation constant<sup>4</sup> as  $1.38 \times 10^{-7}$ . The plot of  $\log D[H]^2$  versus  $\log [DMP]_0$  resulted in a smooth curve with the slope varying from 1 to 2 indicating the formation of both the mono- and di-adducts. The data were analysed to evaluate the nature of adducts and their equilibrium constants as described for the TPPO system. The function  $F_0$  was evaluated and was used to obtain the various constants (Table 1). The *pH* of 50% extraction was about 4.6 in the presence of a mixture of 0.01 *M* each of HBFA and DMP. The adduct formation constant,  $K_{22}$ , was higher in the case of DMP than for quinoline indicating a higher stability of the adduct. However, at higher *pH*, extraction was not significantly higher compared to that of quinoline because of the influence of protonation of DMP which reduces [DMP] in the organic phase.

### (iii) HBFA-TOMACl system

In the extraction of cobalt in the presence of a mixture of HBFA and trioctylmonomethylammonium chloride (TOMACl) a quaternary ammonium salt, the plots of  $\log D$  versus *pH* and  $\log [HBFA]_0$  were linear with slopes of 2.2 and 2.3 respectively. The data showed a variation of distribution ratio with [TOMACl]<sub>0</sub> at low concentrations ( $10^{-5}$  to  $10^{-4}$  *M*) whereas it tended to reach saturation at higher [TOMACl]. From the data obtained at low [TOMACl] the formation of a monoadduct was inferred.

### Adduct formation constants

The data on the extraction of cobalt indicated the formation of synergistic species with various donors. In order to evaluate the adduct formation

constant of  $\text{Co}(\text{BFA})_2$  complex in the organic phase, the equilibrium constants for the reaction.



were evaluated using Eq. (7)

$$K_{2n}^* = K_{2n}/K_{20} \quad \dots (7)$$

The values of various constants are summarised in Table 1.

The adducts formed vary from a monoadduct in the case of sulphoxide, antipyrine and alkyl phosphates to a mixture of both mono- and di-adducts in the case of nitrogen donors. This may be due to the fact that cobalt and copper often exhibit a greater tendency to form a stronger complex with nitrogen donors compared to oxygen donors.

The equilibrium constants for the chelates observed in the present case are in general agreement with the strength of donors as inferred from the extent of adduct formation. The donors can be arranged as  $\text{DPSO} < \text{AP}_3 < \text{EHP} < \text{TBP} < \text{TPPO} < \text{Q} < \text{DMP} < \text{TOMACl}$ . The trend within a group of donors is as expected. In the case of alkyl phosphates, the observed order of stability, viz.  $\text{TBP} > \text{EHP}$ , can be explained on the basis of increased steric effects as the butyl group is replaced by 2-ethylhexyl group. TBP forms a diadduct whereas a monoadduct is indicated with EHP at comparable concentrations. In the case of phosphine oxides, the formation of a diadduct is indicative of greater donor strength of TPPO. Sulphoxides behave as weak donors compared to alkyl phosphates. This has also been observed in other cases and is understandable since both  $\text{P}=\text{O}$  and  $\text{S}=\text{O}$  donors behave essentially as oxygen donors. Among the nitrogen donors, the order observed is  $\text{Q} < \text{DMP}$  which is in agreement with the greater donor strength of DMP as observed in other cases and also indicated by the greater *pK*

Table 1 - Equilibrium constants of cobalt complexes

System	$-\log K_{20}$	$-\log K_{21}^a$	$-\log K_{22}^a$	$\log K_{21}^{*b}$	$\log K_{22}^{*b}$
Co-HBFA	8.13	—	—	—	—
Co-HBFA-TBP	—	—	3.50	—	4.63
Co-HBFA-EHP	—	4.95	—	3.18	—
Co-HBFA-TPPO	—	4.48	2.33	3.65	5.80
Co-HBFA- $\text{AP}_3$	—	5.00	—	3.13	—
Co-HBFA-Q	—	—	1.10	—	7.03
Co-HBFA-DMP	—	3.27	0.40	4.86	7.73
Co-HBFA-DPSO	—	6.20	—	1.93	—
Co-HBFA-TOMACl	—	1.54	—	6.59	—

(a) Equilibrium constant for synergistic extraction (Eq. 2); and (b) adduct formation constant (Eq. 6).

value of DMP compared to that of quinoline. The higher donor strength can be explained on the basis of electron releasing tendency of methyl groups which increase the electron density at the donor nitrogen.

Because of the  $d^7$  structure, cobalt forms both tetrahedral and octahedral complexes with a variety of ligands. This is especially true of complexes with N-donors. The results observed here are, in general, agreement with those reported in literature<sup>5-9</sup> and bring out the greater stabilization of nitrogen adducts compared to those of the oxygen donors.

#### Acknowledgement

The authors wish to thank Dr A K Sundaram for his valuable guidance throughout the course of the work.

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