of these amines can be monomeric. In the case of primene JMT, the slope is 1. The order of extraction obtained was primene JMT > TIOA > THA ≈ LA-2.

The extraction of tris(oxalato)Co(III) decreased with the increase in concentration of primene JMT in xylene, at fixed aqueous phase concentration (0.003 N) of HCl and H₂SO₄. The decrease in the extraction of the complex may be due to amine aggregation which may explain also the low slope value of 1 obtained in the case of primene JMT in earlier experiments.

Somewhat similar results were obtained with 0.01 N H₂SO₄ also. For TIOA and THA, a slope of 3 was obtained. But with primene JMT and LA-2, the extraction was more than 90% even with 0-2% solutions of amines and hence it was difficult to make graphical analysis. The order of extraction was primene JMT ≈ LA-2 > TIOA ≈ THA.

When log E was plotted against log amine (%) in the case of extraction with CCl₄, the slopes were similar to those obtained in the case of toluene but extraction was less.

Extraction with amines using nitrobenzene as the diluent — The amine salts usually exist as ion-pairs in organic diluents of low dielectric constants. The degree of the ion-pair formation depends on the nature of amine salt and the organic diluent. If the ion-pair formation is more in diluents having high dielectric constants, the extraction may also increase. To study this effect, the extraction of tris(oxalato)Co(III) was studied from different HCl solutions into TIOA in nitrobenzene. It was seen that the equilibrium (Eq. 2) shifts completely towards the right hand side. The extraction into 2% TIOA in nitrobenzene, from different HCl solutions, without pre-equilibrating the organic layer, is given in Table 1. It can be seen that the extraction is dependent on the stoichiometric ratio of amine hydrochloride to complex concentration (Table 1).

Extraction into a mixed solvent of toluene and nitrobenzene was studied from 0.003 M HCl by variation method. A plot of E against ratio of nitrobenzene to total volume was linear in the case of TIOA and Amberlite LA-2. For THA, the extraction was similar to that for TIOA in initial stages but afterwards, the effect is not very prominent. Nitrobenzene did not have any effect in the extraction with primene JMT indicating that nitrobenzene has less or negligible influence in systems where amines aggregate.

References

Exchange Studies of Complexes of Co(II) with Oximes of 2-Hydroxyacetophenone, Resacetophenone & 5-Nitroresacetophenone

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Isotopic exchange data of the complexes of Co(II) with 2-hydroxyacetophenone oxime, resacetophenone oxime and 5-nitroresacetophenone oxime in methyl ethyl ketone are reported. In all the three cases the exchange obeyed second order kinetics. The energy of activation in the case of 2-hydroxyacetophenone oxime complex is determined to be 16-55 kcal/mole. Differences in exchange rates were explained in terms of substituent effects.

STUDY of the exchange of metal ions between the complex containing the metal and the free metal ion gives evidence on the nature of bonding in the complex. Exchange reactions of the transition metal complexes with the oximes of 2-hydroxy-
aldehydes have been studied extensively. However, similar studies on 2-hydroxyketoxime complexes have not been made. This prompted us to study the isotopic exchange of Co(II) complexes of the oximes of resacetophenone and 5-nitroresacetophenone.

Resacetophenone oxime was prepared by the method suggested by Dey and Sitaraman. 2-Hydroxyacetophenone (Fluka) was used to prepare its oxime. 5-Nitroresacetophenone oxime was prepared according to the method developed by Omer et al.

Cobalt(II) solution in water was adjusted to pH 7.5 using acetate-borax buffer. Stoichiometric amount of the reagent to form a 1:2 complex in aqueous ethanol was added to the cobalt(II) solution in cold under nitrogen atmosphere. The precipitate was allowed to settle, filtered, washed with warm water and finally with 20% ethanol and dried at 110°C. The composition of the complex was ascertained by estimating cobalt gravimetrically. Methyl ethyl ketone, the solvent used in the exchange study was purified by the method recommended by Walden. Cobalt(II) perchlorate (BDH Analar), sodium perchlorate (E. Merck) were used as such.

Solutions of cobalt(II) perchlorate labelled with 65Co and of the complexes were prepared in methyl ethyl ketone. Sodium perchlorate was used to maintain the ionic strength. Predetermined volumes of the complex and labelled cobalt(II) solutions were mixed and the ionic strength of the mixture adjusted to the desired value. The mixture was kept in a thermostat bath at 30 ± 0.01°C. The course of the exchange was followed by measuring the activity appearing in the initially inactive complex with time after separation from the reactants in the following manner. A 2 ml aliquot of the reaction mixture was withdrawn and treated with 2 ml of water and 0.5 ml of chloroform. Most of the complex was extracted into the methyl ethyl ketone-chloroform layer while cobalt remained in the aqueous phase. The organic phase was separated and washed with the same volumes of water-chloroform and an accurately measured aliquot was transferred to a counting tube. The activity of the samples was measured under the 1.3 MeV photopeak of 65Co using a gamma ray spectrometer type GRS 20B with a single channel analyser and 3.6 x 5.9 cm NaI(Tl) crystal with 1.6 x 3.9 cm well (Trombay Electronic Instruments).

The details of the procedure employed for the calculation of the exchange rates has been reported earlier. The half-times and rates obtained for the exchange of cobalt between the complex and the free cobalt(II) ion for the complexes studied are given in Table 1.

In all the three complexes the exchange reaction was found to obey the second order kinetics. The energy of activation of the exchange process was determined in the case of bis-2-hydroxyacetophenone oxime Co(II) complex from the exchange rates at 30°C and 40°C and the value was found to be 16.55 kcal. These factors indicate that the most probable mechanism for the exchange is the collision between the cobalt ion and the molecule of the complex, similar to that suggested by Calvin and Duffield for the salicylaldoxime derivatives.

As the rates of exchange for the three complexes were determined under identical conditions of temperature, ionic strength and solvent, the differences in the rates of exchange observed could be attributed to the effect of substituents in the ligand. In the case of the bis-resacetophenone oxime Co(II) complex the hydroxyl group in the para position will decrease the electron density due to resonance effect on the chelating nitrogen atom and hence the metal-ligand bonds in this complex would be weaker and the cobalt is expected to exchange faster than that containing unsubstituted ligand. This conclusion is in accordance with the experimental observation. Similar arguments hold good for the bis-5-nitroresacetophenone oxime Co(II) complex. The observed exchange rate is hence in order.

### References


### Determination of Hexacyanoferrate(III)

Using a Mercury Reductor

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The method consists in reducing hexacyanoferrate(III) in 0.5-1.5M hydrochloric acid in a mercury reductor and titrating the ferrate(II) formed with cerium(IV) sulphate (in 0.2-1.0M hydrochloric acid medium) using ferroin as indicator. A mixture of hexacyanoferrate(III) and ferrate(II) can also be analysed by this method using the same oxidant. The method is accurate and convenient.

Numerous methods are available for the titrimetric determination of hexacyanoferrate(III) both in acid and alkaline media. In most