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Zinc Complexing Properties with Dialkylphosphorodithioic Acids

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▶ The composition of the zinc dialkylphosphorodithioate complex which partitions between aqueous acid solutions and CCl_4 has been established as $[(RO)_2PSS]_2Zn$. Characteristic constants have been evaluated; these include the over-all extraction constant, the partition coefficient of the zinc complexes, and the stability constant of the zinc di-*n*-butyl and diisobutyl esters. The extraction mechanism is discussed briefly and the characteristic constants obtained for zinc are compared with those reported for dialkylphosphate complex of zinc.

DIALKYLPHOSPHORODITHIOIC acids have been screened for their extraction of metal ions (*3*) from an acid media, and the behavior of several individual esters of dialkylphosphorodithioic acids have been reported (*8*). The manner in which extractable species form with this class of reagents, and a quantitative evaluation of the extraction characteristics of the zinc complexes were the objects of this study. Few pure sulfur chelate complexes have been fully investigated.

The dialkylphosphorodithioic acids are known to be quite strong acids (*8* and Table I). Among the dialkyl esters there is only a small change in the acid dissociation constant, but a very large change in the partition coefficients. There is no evidence for association of the reagent in the organic phase (*8*).

EXPERIMENTAL

Dialkylphosphorodithioic Acids. Di-*n*-butyl phosphorodithioic acid was obtained from Victor Chemical Co., Chicago, Ill. As received, the reagent was shown to be 99.6% pure by electrometric titration. The ammonium salt of the diethyl ester was obtained from the Monsanto Chemical Co., St. Louis, Mo. Other dialkyl esters were obtained from Lubrizol Corp., Cleveland, Ohio. Esters which required purification were converted to the ammonium salts, followed by extraction of impurities with benzene or CCl_4 and reformation of the acid with addition of mineral acid to the aqueous layer. The free acid may be extracted with CCl_4 and the CCl_4 removed by warming under reduced pressure. The ammonium salts may be recrystallized from ethyl acetate.

Because the free phosphorodithioic acids are somewhat sensitive to hydrolysis, solutions should be prepared fresh each day, or the free acids converted to alkali or ammonium salts.

Determination of Metal Distribution Ratio. The distribution ratio, $D = \frac{|M|_0}{|M|}$, was measured either by use of radiotracers with carriers (*3*) or by titrimetric EDTA methods. Except in strongly acidic solutions, the ionic strength was maintained at 1.0.

Extractions were performed with a Burrell wrist-action shaker by shaking equal volumes (10 ml.) of the organic and aqueous phases for 10 minutes at 25° ± 2° C. in separatory funnels of conventional design. Preliminary ex-

Table I. Characteristic Constants for Zinc Dialkylphosphorodithioates

System: CCl_4–aqueous acid medium

Ester	log K^*	log K_cP_c	log P_r	pK_a	log P_c	log K_c
Diethyl	ca. −10	ca. −9.3	0.45	−0.10	...	...
Di-*n*-butyl	1.22	6.57	2.52	0.22	2.77	8.81
Diisobutyl	1.29	5.77	2.63	0.10	2.70[a]	4.00
Di-*sec*-butyl	1.37	...	...	...	2.77[a]	...
Di-(2-ethyl)hexyl	1.40	...	...	...	2.86[a]	...

[a] Estimated from extrapolation parallel to the complete distribution curve for di-*n*-butyl ester on logarithmic coordinates.

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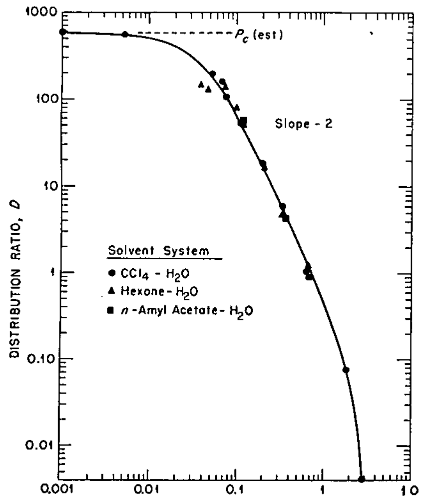

Figure 1. Effect of carrier diluent upon the distribution ratio of zinc (0.0154M) from aqueous HCl medium with 0.207M di-n-butyl phosphorodithioic acid

Loading corrections have been made

periments indicated that the distribution equilibrium was achieved within 10 minutes.

RESULTS

Effect of Carrier Diluent. The distribution of zinc was studied as a function of pH in three solvent systems: CCl_4–water, methyl isobutyl ketone–water, and *n*-amyl acetate–water. Di-*n*-butylphosphorodithioic acid concentration was identical in each system. As shown in Figure 1, the curves, log *D* *vs.* log [H$^+$], are essentially superimposed, although small differences in the distribution ratio do exist and were reported earlier (*3*) for a number of solvents. There is no indication that significant complexes form between species containing zinc and carrier diluent molecules unless a similar mixed complex is formed with each solvent, which is not likely in view of their marked structural differences.

Identification of Phase Species. The composition of the zinc di-*n*-butylphosphorodithioate complex was established by studying the distribution of the metal at different concentrations of the free ligand (Figure 2) and at different concentrations of hydrogen ion (Figure 3), in each case with several different concentrations of reagent, $[HR]_o$, in the organic solvent layer. Data for the diethyl ester are included in Figure 2. The ascending portions of Figures 2 and 3 possess slopes of 2 and −2, respectively. In Figure 2 the aqueous ligand concentration was computed from the relationship

$$[R^-] = ([HR]_{o,\,\text{initial}} - 2\,[ZnR_2]_o)K_a/[H^+]\,P_r \quad (1)$$

where K_a is the acid dissociation constant and P_r, the partition coefficient of the reagent (Table I and *8*).

Since for zinc the coordination number is twice the charge, the appropriate number of bidentate ligands will both neutralize the metal ion charge and completely destroy the primary hydration shell, transforming the hydrated ion into an unhydrated organic molecule, the extractable species, $ZnR_{2(o)}$

$$Zn(OH_2)_4{}^{+2} + 2HR_{(o)} \rightleftarrows ZnR_{2(o)} + 2H^+ + 4H_2O \quad (2)$$

At the low concentrations of zinc employed, 0.008 to 0.015*M*, it seems certain that the zinc ions exist initially as a mononuclear species in the aqueous phase. Hydrolysis species [such as Zn(OH)$^+$] can be ignored in the pH interval 0 to 7.6. Absence of an intermediate ZnR$^+$, except in the vicinity of the "knee" in Figures 2 and 3, or complexes such as $Zn(OH)R_{(o)}$ and $ZnR_2(HR)_{n(o)}$ in the organic phase, is proved by the manner in which *D* varies with [H$^+$] and [R$^-$] for the different initial reagent concentrations (*6*, *7*); in particular, by the convergence of the distinct isograms of Figure 3 to a common plateau.

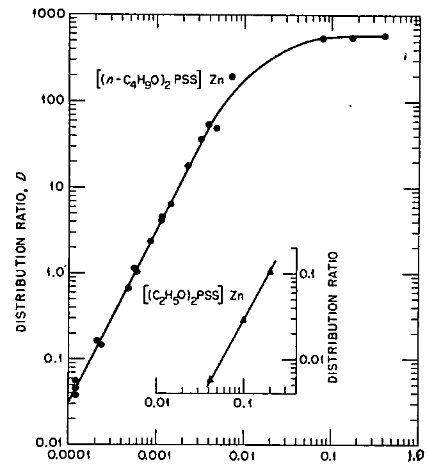

Figure 2. Distribution of zinc as a function of aqueous ligand concentration at several concentrations of hydrogen ion for di-*n*-butyl phosphorodithioic acid (upper curve) and for diethyl phosphorodithioic acid (lower curve)

Evaluation of Characteristic Constants. The extraction constant (K^*) for the partition equilibrium (Equation 1) is given by

$$\log K^* = \log [ZnR_2]_o + 2 \log [H^+] - 2 \log [HR]_o - \log [Zn^{+2}] \quad (3)$$

On the ascending rectilinear portions of the curves in Figures 1–4, the distribution ratio is given by

$$D \simeq \frac{[ZnR_2]_o}{[Zn^{+2}]} \quad (4)$$

to a good approximation and, therefore,

$$\log K^* = \log D + 2 \log [H^+] - 2 \log [HR]_o \quad (5)$$

Also,

$$K^* = K_c P_c (K_a/P_r)^2 \quad (6)$$

where K_c is the formation constant and P_c the partition coefficient of the metal complex.

The value of the extraction constant can be obtained by substituting the appropriate experimental quantities into Equation 3. From the horizontal portions of Figures 2 and 3, the value of the partition coefficient, $P_c = [ZnR_2]_o/[ZnR_2]$, can be estimated. These values, plus values for the acid dissociation constant and the partition coefficient of the reagent which were determined earlier (*8*), enable the formation constant to be calculated (Equation 6). These characteristic constants are given in Table I for a number of zinc dialkylphosphorodithioate complexes.

Values for the partition coefficients of the diisobutyl-, di-*sec*-butyl-, and di-(2-ethyl)hexyl phosphorodithioate complexes were estimated from extrapolation parallel to the complete distribution curve for the di-*n*-butyl complex on logarithmic coordinates (Figure 4).

DISCUSSION

The mechanism of the zinc ion extraction into dilute solutions of the dialkylphosphorodithioic acids in carbon tetrachloride is a normal metal chelation without the added complication of solvating reagent molecules or the

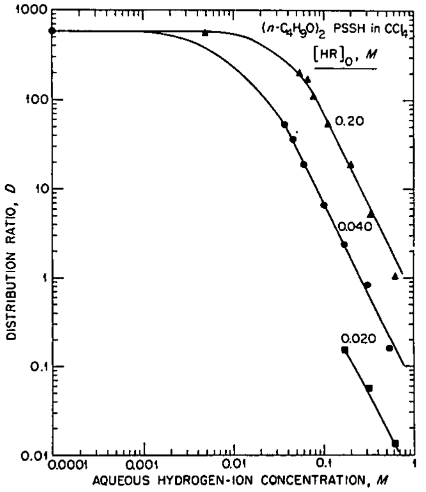

Figure 3. Distribution of zinc as a function of aqueous HCl concentration for three different concentrations of di-*n*-butylphosphorodithioic acid present in CCl_4

existence of dimeric forms of these reagents in the nonpolar solvent.

In progressing from the diethyl ester to esters with longer chain alkyl groups, there occurs a marked increase in the extractability. Inspection of a Stuart-Briegleb model of the zinc dialkylphosphorodithioate complex provides a possible explanation. When the linear portion of the alkyl chain exceeds two carbon atoms, normal rotation about the carbon–carbon bonds provided a protective screen around the central metal atom, restricting access of solvent or solute molecules to the site. Branching in the alkyl group increases the extractability to a slight extent, paralleling the small increases in acidity observed for the parent reagents (*8*).

The stability constant of the zinc complexes provides quantitative evidence for appreciable stability of the phosphorodithioate complex. Data are lacking for a direct comparison with dialkylphosphates. However, the extraction constant for the zinc di-(2-ethyl)-hexylphosphorodithioate is 25 as compared with a value of 0.056 reported for zinc di-(2-ethyl)hexylphosphate, which is probably $ZnR_2(HR)_2$ in the organic phase (*4*, *5*), an increase in extractability by a factor of 450. Conceivably the larger radii of the sulfur atoms permits the formation of a 4-membered ring with the central zinc ion with less strain and distortion of bond angles (*1*, *2*).

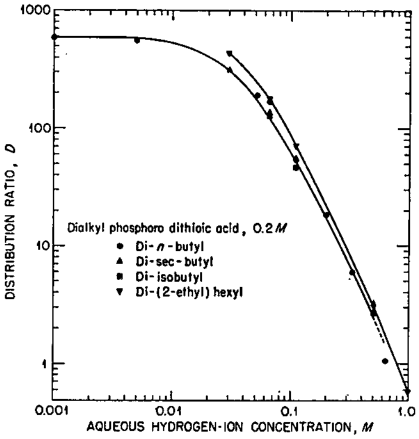

Figure 4. Distribution of zinc as a function of aqueous HCl concentration for four esters of phosphorodithioic acid, each 0.2*M* in CCl_4

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