When data are equally spaced on the t axis, the nonlinear regression method yields reliable results at potential-step widths as large as 0.10 s, where linear plots may lead to qualitative errors. The diagnostic test for reactant adsorption based on deviation-pattern recognition can be used at step widths up to at least 0.50 s, where acceptable values of surface concentration can be obtained by clustering the data in regions of highest relative weight. Such experiments at larger τ may become important when it is desired to study adsorption and homogeneous chemical reactions simultaneously (*17*).

Qualitative trends derived from pointwise variance analysis in this work are expected to be general. The computations were done for a fairly representative surface concentration, 10^{-10} mol cm^{-2}. Standard errors for a given experimental system can be estimated from those in Tables IV and VII if an estimate of the standard error in Q is available (*8*). Predictions of standard errors and relative weights will differ, of course, for systems with slow adsorption or redox equilibrium, for which modifications in the model are necessary. Finally, although only reactions featuring diffusion and reactant adsorption were investigated in this study, the approach presented is a general one, is independent of the geometry of the electrode, and should be applicable to analysis of more complex electrochemical systems, when the proper models are used.

Registry No. $NaNO_3$, 7631-99-4; KSCN, 333-20-0; Hg, 7439-97-6; Tl, 7440-28-0; U, 7440-61-1; Cd, 7440-43-9.

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Hydrolysis of the *O*,*O*-Dialkyl Phosphorodithioic Acids Used as Extractants in Liquid–Liquid Systems

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At 25 °C, the title compounds are fairly stable against hydrolysis: the yield of hydrolysis of the bis(2-ethylhexyl) phosphorodithioic acid (DEHPDTA) is less than 10% after 5 months in contact with H_2O or 1 M HCl. The rate of hydrolysis is particularly dependent on the temperature: the half-life of a 0.5 M solution of DEHPDTA is about 80 days at 35 °C, 24 h at 65 °C, and only 1 h at 100 °C. In contrast with their acidic forms, the dialkyl phosphorodithioates (as a salt of sodium or engaged in metal complexes) are stable. Increase in the hydrophobic feature of the alkyl groups enhances the stability; however, even the didodecyl phosphorodithioic acid is rapidly hydrolyzed above 40 °C. Finally, the replacement of the alkyl groups by aryl groups dramatically enhances the tendency for hydrolysis. For the bis(2-ethyhexyl) phosphorodithioic acid, the reaction of hydrolysis mainly gives $H_2S\uparrow$, H_3PO_4, 2-ethylhexanol, and the bis(2-ethylhexyl) phosphorothioic acid.

Organophosphorus compounds, both neutral and acid, have been extensively used as extractants for metallic species. Their analogues, wherein one or more sulfur atoms have replaced oxygen atoms, have also been investigated. Among them, the dialkyl phosphorodithioic acids have attracted great attention. Indeed, the phosphorodithioates are soft bases which react preferentially with soft or borderline acids and consequently can selectively extract cations such as Ni^{2+} or Zn^{2+} (borderline acids) from acidic leaching solutions or heavy metals (Hg^{2+}, a soft acid) from acidic effluents (*1–6*). Moreover, the dialkyl phosphorodithioic acids are cheap and present only a low toxicity. The dialkyl phosphorodithioic acids are easily synthesized by the straightforward reactions of alcohols with phosphorus pentasulfide (yield up to 90%) (*3, 7*)

$$4ROH + P_2S_5 \rightarrow 2(RO)_2P(=S)SH + H_2S$$

These compounds are stronger acids ($pK_a \sim 1$ (*8*)) than the dialkylphosphoric acids, and conversely to the latter, they have almost no tendency to form dimeric species in organic solution (*8, 9*). The short-chain derivatives, e.g., the diethyl phosphorodithioic acid, are far too soluble in aqueous phases to receive any application in the solvent extraction area. On the other hand, the distribution coefficients of the long-chain derivatives are high. For instance, the distribution coefficient of the bis(2-ethylhexyl) phosphorodithioic acid between water and organic solvents such as carbon tetrachloride, heptane, or benzene is about $10^{5.4}$ (*8*).

Although the dialkyl phosphorodithioic acids or their salts have found important applications as flotation reagents

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(Aerofloat), as extreme-pressure additives in lubricating oils, or as starting materials for the synthesis of insecticides (parathion, methylparathion), they have never been used commercially for the concentration and purification of metallic species by liquid–liquid extraction because of the suspicion of poor stability. The stability of the dialkyl phosphorodithioic acids, a determining parameter for any large scale use, must be considered with respect to two main phenomena: their oxidation and their hydrolysis. For the oxidation, it is of interest to note that the reduction potential of di-*n*-butyl phosphorodithioic acid is +0.47 V/NHE (*10*). Such a value explains why strong oxidants such as 7–9 M HNO_3, H_2O_2, Br_2, Tl(III), Cr(VI), Fe(III), etc. react with the dialkyl phosphorodithioic acids with formation of disulfides, $(RO)_2P(=S)SS(S=)P(OR)_2$ (*11*). Consequently contact with strong oxidizing agents should be carefully avoided. As for hydrolysis, Bode (*12*) has studied the decomposition of diethyl phosphorodithioic acid in solutions that contained hydrochloric or sulfuric acid in various concentrations. He reported that the half-life of diethyl phosphorodithioic acid at room temperature in 1 M HCl is 250 h and in 10 M HCl only 4.8. The decomposition is a first-order reaction. Such results suggest that the dialkyl phosphorodithioic acids are not very stable against hydrolysis. In fact, the stability of these compounds would be closely related to the hydrophobic feature of their alkyl groups (*13*), and according to Levin (*3*) the derivatives such as the bis(2-ethylhexyl) phosphorodithioic acid would be fairly stable in the absence of oxidant; i.e., their extraction capacity would not vary with time. Although it seems reasonable to admit that the long-chain derivatives are distinctly more stable against hydrolysis than the short-chain ones, little evidence of this is given in the literature.

Considering on the one hand the potential interest of the long-chain dialkyl phosphorodithioic acids in hydrometallurgy, and on the other hand the absence of reliable and comprehensive bibliographical data, we have decided to investigate their stability in liquid–liquid systems. The study has been mainly performed with the bis(2-ethylhexyl) phosphorodithioic acid, which is a slightly viscous liquid at room temperature, but comparisons have been made with three other derivatives corresponding to R = *n*-butyl, *n*-dodecyl, and 4-nonylphenyl, respectively.

EXPERIMENTAL SECTION

Reagents. All aqueous solutions were prepared from reagent grade metallic salts. Di-*n*-butyl, di-*n*-dodecyl, and bis(4-nonylphenyl) phosphorodithioic acids were synthesized from phosphorus pentasulfide (Fluka) and pure alcohols: 1-butanol (Hopkins and William), 1-decanol (Prolabo), and 4-nonylphenol (Fluka), respectively. They have been used without purification considering that in all cases synthesis yield is close to 90–95%. Bis(2-ethylhexyl) phosphorodithioic acid is a commercially available product (Melioran S4070 from Gerland). Two qualities have been tested: quality A (content about 83%, the main impurity is 2-ethylhexanol) and quality B (absence of 2-ethyhexanol. Found (Calcd): C, 54.84 (54.24); H, 9.53 (9.89); S, 17.66 (18.08); P, 8.81 (8.76)). Exsol D100 (Esso) used as diluent is an aliphatic (99.1%) petroleum fraction (flash point 102 °C).

Apparatus pH measurements were performed with a TB/HS glass electrode, a C10 calomel electrode reference, and a PHN75 pH meter (Tacussel, Paris). The spectrometric instruments used were a Perkin-Elmer Model 298 for IR spectra and a Varian EM 390 (^1H) and a Varian FT 80A (^1H, $^{31}P\{^1H\}$) for NMR measurements. Chemical shifts (δ) are referenced to Me_4Si (^1H) or to an 85% orthophosphoric acid external standard (^{31}P). Mass spectra were recorded by the Laboratoire de Spectrométrie de Masse (ENSCP, Paris) with a Ribermag 10-10 mass spectrometer.

Analytical Methods. Microanalysis were performed by the Service Central d'Analyse (CNRS, Vernaison). Nickel(II) titrations in aqueous phases were carried out volumetrically with EDTA.

The stability of the dialkyl phosphorodithioic acids (HL) against hydrolysis was studied by shaking these reagents (as pure liquids or in solution in an inert diluent) with various aqueous phases at different temperatures. The reaction was performed either in the air or under nitrogen. The degradation of the reagent was followed by examining any change in the composition of the aqueous phase, by determining the nature and the quantity of gas evolution, and by analyzing the remaining organic layer (microanalysis, acidimetry, IR, ^1H, and ^{31}P NMR, mass spectrometry).

Table I. Influence of the Nature of the Aqueous Phase on the Hydrolysis Rate of Bis(2-ethylhexyl) Phosphorodithioic Acid in Solution (0.47 M) in Exsol D100, at 65 °C[a]

time, h	HCl 4 M	HCl 2 M	HCl 0.5 M	H_2O	NaOH[b] 2 M	NaOH[b] 4 M
24	0.54	0.43	0.45	0.46	0.98	1.00
48	0.20	0.15	0.17	0.22	1.00	1.00
134	0	0	0	0	1.00	0.99

[a] The results are expressed as X_{HL} (proportion of nondegradated reagent). [b] Sodium hydroxide concentration in the aqueous phase after neutralization of bis(2-ethylhexyl) phosphorodithioic acid.

Moreover a rapid determination of the yield of decomposition was based on extraction of nickel(II) at pH ≃2 and the result was expressed as $X_{HL} = [Ni]_{org}^t/[Ni]_{org}^0$. $[Ni]_{org}^t$ is the concentration of nickel(II) extracted at 25 °C (2 h of mixing) from an aqueous solution of $NiSO_4$ (50 g/L) into an equal volume of a dialkyl phosphorodithioic acid solution. The latter was either the degradated organic layer itself (after *t* hours of treatment) or a solution prepared by diluting this organic layer in Exsol D100. $[Ni]_{org}^0$ is identical to $[Ni]_{org}^t$ but at $t = 0$ (i.e., before any decomposition takes place).

Under the conditions chosen for the extraction of nickel(II), $[Ni]_{org}^0$ and $[Ni]_{org}^t$ correspond to the plateau of the distribution curves $[Ni]_{org} = f[Ni]_{aq}$ (i.e., $[Ni]_{org} \simeq [HL]_{org}/2$) (*14*).

Consequently the coefficient X_{HL} gives a good estimation of the proportion of nondegradated extractant: $X_{HL} \simeq [HL]_{org}^t/[HL]_{org}^0$. It must be pointed out that Ni(II) reacts selectively with the dialkyl phosphorodithioic acids at pH 2. Indeed, the degradation compounds, especially the chelating dialkyl phosphorothioic acids, do not extract Ni(II) at such a acidity.

RESULTS AND DISCUSSION

(1) Influence of Various Parameters on the Hydrolysis of Long-Chain Dialkyl Phosphorodithioic Acids (in Collaboration with Martine Caldentey). The temperature has been found to be a key parameter for the degradation of the dialkyl phosphorodithioic acids. Indeed, at room temperature the yield of degradation of bis(2-ethylhexyl) phosphorodithioic acid (DEHPDTA) is less than 10% after 5 months in contact with H_2O or 1 M HCl. But its half-life ($t_{1/2}$) in solution in Exsol D100 is about 80 days at 35 °C, 24 h at 65 °C and only 1 h at 100 °C. Such a degradation is not a mere thermal decomposition but a reaction of hydrolysis since in the absence of any contact with water the reagents do not significantly decompose, even after 24 h at 85 °C or 1 week at 65 °C.

The results given in Table I show that the acidity of the aqueous phase, from pure water up to 4 M HCl, has only a little influence on the hydrolysis rate of bis(2-ethylhexyl) phosphorodithioic acid in solution in Exsol D100. In all this range of acidity, the hydrolysis is rapid above 40 °C. On the other hand, and as previously reported for the diethyl phosphorodithioic acid (*12*), the formation of the sodium bis(2-ethylhexyl) phosphorodithioate by addition of sodium hydroxide appears to efficiently prevent the reaction of hydrolysis.

Another significant result is that the bis(2-ethylhexyl) phosphorodithioate engaged in metal complexes such as $Ni(DEHPDTA)_2$ is totally stable against hydrolysis, even in slightly acidic media (pH ~3) (in highly acidic media the metal cations are stripped).

Table II. Balance for Sulfur and Phosphorus[a]

test	0 $t = 0$	1 $t = 13^1/_2$ h 65 °C	2 $t = 41$ h 65 °C	3 $t = 169$ h 65 °C	4 $t = 333$ h 65 °C	5 $t = 167$ h 100 °C (reflux)
S, g (%)						
S as H_2S[b]		0.52 (29.4%)	1.12 (63.3%)	1.28 (72.3%)	1.27 (71.8%)	1.29 (72.9%)
S in the organic phase	1.77	0.99 (55.9%)	0.44 (24.9%)	0.38 (21.5%)	0.39 (22.0%)	0.24 13.6%)
S[c] total	1.77	1.51 (85.3%)	1.56 (88.2%)	1.66 (93.8%)	1.66 (93.8%)	1.53 (86.4%)
P, g (%)						
P as H_3PO_4		0.26 (29.5%)	0.42 (47.7%)	0.49 (55.7%)	0.50 (56.8%)	0.63 (71.6%)
P in the organic phase	0.88	0.59 (67.0%)	0.42 (47.7%)	0.39 (44.3%)	0.37 (42.0%)	0.23 (26.1%)
P total	0.88	0.85 (96.5%)	0.84 (95.4%)	0.88 (100%)	0.87 (98.8%)	0.86 (97.7%)
S/P[d]	1.94	1.63	1.02	0.94	1.03	0.98

[a] Corresponding to a 10-g sample of DEHPDTA (quality B). [b] Recovered as a white precipitate of zinc sulfide. [c] The recovery of S is less than 100% probably because of hydrogen sulfide losses. [d] Moles of S/moles of P in the organic phase.

The quality of the reagent (A or B, see Experimental Section) and the nature of the atmosphere in the reactional flask (nitrogen or air) have no influence.

Increase in the hydrophobic feature of the alkyl groups decreases the tendency for hydrolysis: $C_2H_5 \gg C_4H_9$ ($t_{1/2} \simeq$ 4 h at 65 °C) > C_8H_{17} ($t_{1/2} \simeq$ 24 h at 65 °C). However, even with longer chains such as *n*-dodecyl the degradation is rapid at 65 °C; but because of emulsion formation it has not been possible to measure the half-life times by nickel(II) extraction. The replacement of the alkyl groups by the hydrophobic 4-nonylphenylone dramatically enhances the tendency for hydrolysis: $t_{1/2} < 1$ h (65 °C) instead of 24 h for DEHPDTA. Finally, a rapid study performed with the di-*n*-butyl and the bis(4-methylphenyl) phosphinodithioic acids has shown that the phosphinodithioic acids, $R_2P(=S)SH$, the extractive properties of which are similar to the ones of the dialkyl phosphorodithioic acids, are also poorly stable against hydrolysis at high temperature.

(2) Degradation Compounds Formed by Hydrolysis of Bis(2-ethylhexyl) Phosphorodithioic Acid. To identify more easily the decomposition compounds, the bis(2-ethylhexyl) phosphorodithioic acid (quality B) has been used undiluted.

As the reaction of hydrolysis was in progress no spectacular phenomena were observable except a bad smelling hydrogen sulfide evolution which was more intense at higher temperatures.

Analysis (acidimetry, gravimetry of ammonium phosphomolybdate, ^{31}P NMR) of the aqueous phases has proved that only orthophosphoric acid was released in water in appreciable quantities.

A relevant point is that the evolution of H_2S and the formation of H_3PO_4 cease before all the sulfur and the phosphorus initially present in the sample of DEHPDTA be transformed into H_2S and H_3PO_4, respectively (Table II).

The organic layers obtained after hydrolysis were clear, colorless, and slightly viscous. They contained both 2-ethylhexanol (for a 10-g sample of DEHPDTA (B), up to 3 g of pure 2-ethylhexanol (IR, ^1H NMR, microanalysis) was isolated) and a compound (or a mixture of compounds) fairly stable against hydrolysis and characterized by a ratio mole of S/mole of P equal to one (Table II). Further identification has been made as reported below.

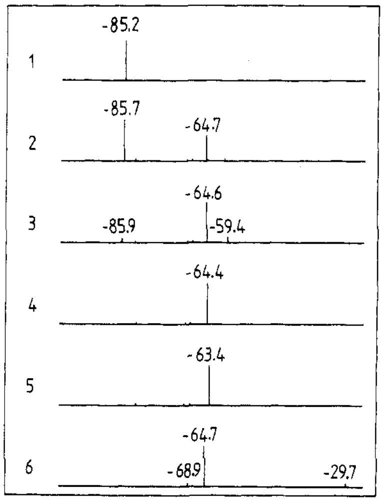
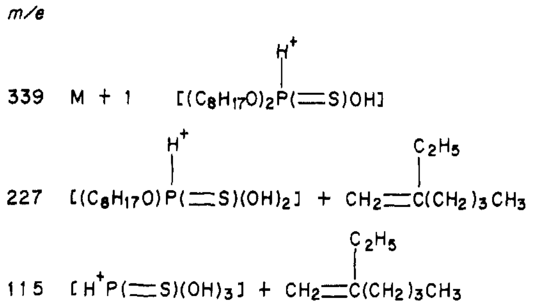


Figure 1. Proton-decoupled ^{31}P NMR spectra at 28 °C: (1) DEHPDTA [quality B]; (2) organic layer test 1 [65 °C, $13^1/_2$ h]; (3) organic layer test 2 [65 °C, 41 h]; (4) organic layer test 3 [65 °C, 169 h]; (5) organic layer test 4 [65 °C, 333 h]; (6) organic layer test 5 [reflux, 167 h]. The spectra were recorded on undiluted phases and the chemical shifts (δ_{ppm}) are referenced to an 85% orthophosphoric acid external standard.

(a) Investigation of the Oil without Separation. The proton-decoupled ^{31}P NMR spectra of the various organic phases have been recorded (Figure 1). The spectrum of bis(2-ethylhexyl) phosphorodithioic acid contains a single peak at −85.2 ppm (the literature gives δ_P between −85 and −86 ppm for $(RO)_2P(=S)SH$ with R = C_2H_5, C_3H_7, C_4H_9, and C_5H_{11} (*15, 16*)).

As the reaction of hydrolysis progresses the peak close to −85 ppm is replaced by a peak near −64 ppm. In fact, several other minor peaks are observable. For the oil completely hydrolyzed at 65 °C (tests 3 and 4) the height of the three additional peaks at −82.5, −70.0, and −68.8 ppm is only between 2% and 4% of the height of the peak at −64 ppm. For the oil hydrolyzed at reflux temperature only two additional peaks are present (−68.9 and −29.7 ppm) but they are slightly more intense (11% and 8% of the height of the peak at −64 ppm, respectively). Such observations suggest that the reaction of hydrolysis gives apart from $H_2S\uparrow$, H_3PO_4, and 2-ethylhexanol

Chart I



$$\begin{array}{lll} m/e & & \\ 339 & M+1 & [(C_8H_{17}O)_2\overset{H^+}{P}(=S)OH] \\ 227 & & [(C_8H_{17}O)\overset{H^+}{P}(=S)(OH)_2] + CH_2=\overset{C_2H_5}{C}(CH_2)_3CH_3 \\ 115 & & [H^+P(=S)(OH)_3] + CH_2=\overset{C_2H_5}{C}(CH_2)_3CH_3 \end{array}$$

a main phosphorus-containing compound P ($\delta \sim -64$ ppm) and smaller quantities of some other organophosphorus derivatives, the number and the nature of which depend on the temperature. For all these compounds including P there is no phosphorus–phosphorus coupling.

From bibliographical data we deduce that (i) P could be a *O,O*-dialkyl phosphorothioic acid (the literature (*15, 17*) gives δ_P -64 ppm for $(RO)_2P(=S)OH$ with R = C_2H_5 and C_3H_7) and (ii) the two byproducts giving rise to the peaks at -68.9 and -29.7 ppm on the ^{31}P NMR spectra of the oil obtained at reflux temperature (test 5) could be a *O,O,O*-trialkyl phosphorothioate and a *O,O,S*-trialkyl phosphorothioate, respectively (the literature gives δ_P -67 to -68.5 ppm for $(RO)_3P=S$ (*15, 16*) and δ_P -28 ppm for $(RO)_2P(=O)SR$ (*15, 17*) with R = C_2H_5 and C_3H_7).

The acidimetric titration curves (titration by 0.1 M NaOH in 1:2 water/acetone mixtures) of the organic layers recovered after hydrolysis (tests 3, 4, and 5) exhibit a single acidity. The oils hydrolyzed at 65 °C liberate about 1 mole of hydrogen ions per mole of phosphorus atoms (for instance 0.95 for test 4) as expected from the formation of almost exclusively $(RO)_2P(=S)OH$. In fact the difference between 0.95 and 1.00 put in evidence the presence of about 5% of neutral organophosphorus derivatives. On the other hand, the organic layer hydrolyzed at reflux temperature (test 5) liberates only 0.82 mol of hydrogen ions per mole of phosphorus atoms, which is an argument in favor of the formation of the neutral $(RO)_3P=S$ and $(RO)_2P(=O)SR$ species. It must be pointed out that $(RO)_3P=S$ can be formed by a mere reaction of esterification between $(RO)_2P(=S)OH$ and 2-ethylhexanol. For the organic layers for which a ^{31}P NMR signal appears at -59.4 ppm (tests 1 and 2), an additional equivalent point related to a much weaker acidity ($pK_a \sim 8$ in the water/acetone mixture) is observable on the titration curves. Such an equivalent point could be due to the titration of the second acidity of a monoalkyl phosphorothioic acid $(RO)P(=S)(OH)_2$.

(*b*). *Attempt of Separation.* The main organophosphorus decomposition product P has been isolated by chromatography of its salt of sodium on a column of Kiesel Gel 60 (230–400 mesh ASTM, Merck) and reacidification.

Microanalysis data (found (calcd): C, 56.03 (56.80); H, 10.64 (10.35); O, 15.14 (14.20); S, 9.39 (9.48); P, 9.04 (9.16)), IR (curve 7 in Figure 2) and ^1H NMR spectra are consistent with the bis(2-ethylhexyl) phosphorothioic acid $(C_8H_{17}O)_2P(=S)OH$. This conclusion is confirmed by the mass spectrum (see Chart I). A peak observable at 677 corresponds to 2M + 1.

As a conclusion we can say that the long-chain dialkyl phosphorodithioic acids are significantly more stable against hydrolysis than the short-chain ones. At room temperature compounds such as the bis(2-ethylhexyl) phosphorodithioic acid could be used commercially for the concentration and purification of metallic species by liquid–liquid extraction. However, great care should be taken to control the temperature.

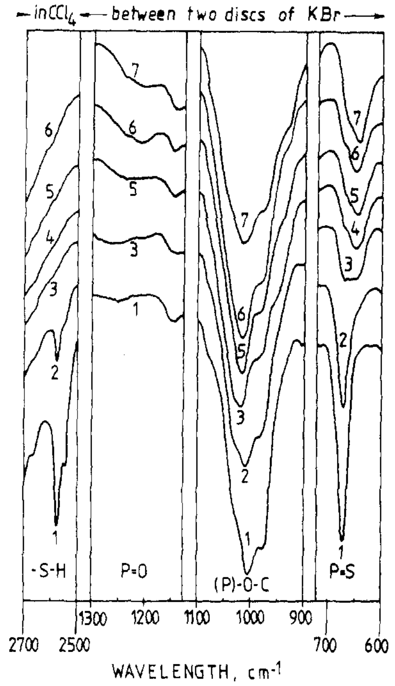
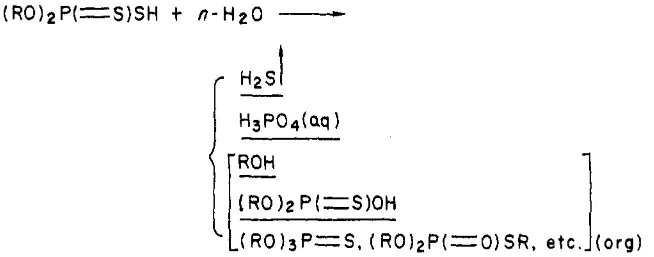


Figure 2. Infrared absorption spectra: (1) DEHPDTA [quality B]; (2) organic layer test 1 [65 °C, 13$^1/_2$ h]; (3) organic layer test 2 [65 °C, 41 h]; (4) organic layer test 3 [65 °C, 169 h]; (5) organic layer test 4 [65 °C, 333 h]; (6) organic layer test 5 [reflux, 167 h]; (7) compound P.

The reaction of hydrolysis of bis(2-ethylhexyl) phosphorodithioic acid can be summarized by



$$(RO)_2P(=S)SH + n\text{-}H_2O \longrightarrow \left\{ \begin{array}{l} \underline{H_2S}\uparrow \\ \underline{H_3PO_4(aq)} \\ \left[\begin{array}{l} \underline{ROH} \\ \underline{(RO)_2P(=S)OH} \\ (RO)_3P=S,\ (RO)_2P(=O)SR,\ etc. \end{array} \right]_{(org)} \end{array} \right.$$

where the underlined species correspond to the main decomposition compounds. The bis(2-ethylhexyl) phosphorothioic acid formed by the above reaction is significantly more stable against hydrolysis than DEHPDTA. The chelating properties of the dialkyl phosphorothioic acids have been reported by Handley (*18*).

Registry No. H_2S, 7783-06-4; H_3PO_4, 7664-38-2; DEHPDTA, 57876-21-8; didodecyl phosphorodithioic acid, 6028-51-9; dibutyl phosphorodithioic acid, 2253-44-3; bis(4-nonylphenyl)-phosphorodithioic acid, 57343-17-6; 2-ethylhexanol, 104-76-7; bis(2-ethylhexyl)phosphorothioic acid, 17618-27-8.

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Spectrophotometric and Titrimetric Determination of Carboxylic Acid Anhydrides

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Two redox methods are described for the determination of carboxylic acid anhydrides involving reaction with either an excess of 4-aminophenol or a measured but excessive amount of sulfanilamide and photometric titration of *N*-acyl-4-aminophenol with 2-iodylbenzoate by measuring the absorbance of orange-red product at 444 nm or the residual amount of sulfanilamide is determined by titration with chloramine-T in the presence of acidified potassium bromide using methyl red as visual indicator. Mixtures of certain anhydrides have also been analyzed by the 2-iodylbenzoate method. The methods are rapid, precise, and accurate. No correlation is needed if carboxylic and mineral acids are also present. Carboxylic acid chlorides also react quantitatively.

Earlier methods for carboxylic acid anhydrides were based on acid–base titrations making necessary a correction in anhydride content due to acid present. Simultaneous measurement was made by titrating the originally present acid plus that produced on hydrolysis of anhydride and then determining the anhydride from difference to a second titration of the sample with either sodium methoxide or alkali hydroxide after pretreatment of the test sample with aniline (*1*). Reaction with morpholine (*2–4*) or aniline (*5*) followed by titration of residual amine assays the anhydride independent of carboxylic acid impurities. However, limitations are due to maleic and citraconic anhydrides, as their acids (and others with ionization constant greater than 2×10^{-2}) are acidic to visual indicator (*2*), and unsaturated anhydrides which undergo addition reaction with excess morpholine (*4*). The aniline method is free from such shortcomings but the reaction with succinic anhydride occurs under vigorous conditions so that the initially produced anilide and any free succinic acid present also combine with aniline (*5*). Mineral acids interfere in both of the amine methods. In the presence of large excesses of anhydrous acetic acid, the resultant amide tends to buffer the end point in the determination of acetic anhydride (*2*). Formation of hydroxamic acid and color development with iron(III) has been used for organic esters, acid halides, anhydrides, and lactones (*6*). The calibration curves are not always linear with anhydrides (*1*).

Two methods are described in the present paper which make use of redox reactions and are free from the difficulties mentioned above. It is observed that 4-aminophenol undergoes acylation exclusively at its amino group when an excess of it is made to react with carboxylic acid anhydrides. The *N*-acyl-4-aminophenol produces almost instantaneously an orange-red color on oxidation with 2-iodylbenzoate that absorbs maximally at 444 nm. The titration can be followed by measuring the color produced. The second method also involves acylation of an aromatic amino group but now of the sulfanilamide which after acylation fails to undergo its typical disubstitution reaction with bromine (*7*). The amount of sulfanilamide consumed in acylation, as found by titration with chloramine-T in the presence of acidified potassium bromide, is a measure of anhydride.

EXPERIMENTAL SECTION

Reagents. 2-Iodylbenzoate, 0.01 M solution, was prepared by dissolving 2.8 g of the free acid reagent (synthesized by the method of Banerjee et al. (*8*)) in a slight molar excess of potassium hydroxide (0.7 g in 50 mL of water) and diluting to 1 L with water. It was standardized iodometrically

$$O_2IC_6H_4CO_2^- + 4I^- + 5H^+ \rightarrow 2I_2 + IC_6H_4CO_2H + 2H_2O$$

Alternatively, a known amount of analytical reagent grade paracetamol (*N*-acetyl-4-aminophenol) is photometrically titrated with the reagent (as described below), the two substances reacting on a 1:1 molar ratio. The strength of 2-iodylbenzoate determined by two methods agreed within 0.2%.

Chloramine-T, 0.02 M solution, was made by dissolving 5.62 g of sodium *N*-chloro-4-toluenesulfonamide trihydrate in 1 L of water and standardizing the solution iodometrically (*9*).

Sulfanilamide, 0.01 M solution (about 0.43 g), was dissolved in 250 mL of ethanol. Prestandardization is not necessary as a reference titration on the same volume of this solution is also carried out along with the analysis.

4-Aminophenol was a 2% solution in ethanol.

Methyl red was a 0.02% indicator solution in ethanol.

Apparatus. A Pye-Unicam SP 8-100 spectrophotometer was used.

Samples. All anhydride samples were purified by either distillation or recrystallization, and their purity was checked by established methods (Tables I and II).

Procedures. *Photometric Titration with 2-Iodylbenzoate.* An accurately weighted amount of sample containing about 1 mmol of anhydride is combined with 10 mL of 2% 4-aminophenol and warmed in a boiling water bath for a minute, except for phthalic and camphoric anhydrides where heating for 10 min under reflux is necessary. The contents are cooled to room temperature and diluted to volume in a 100-mL calibrated flask with ethanol or acetone. Two to 5 mL portions of this solution are mixed in a photometric cell with 20 mL of acetone and 5 mL of 5% sulfuric acid and diluted to 50 mL with water. The absorbance of solution is set to zero or minimum at 444 nm and it is titrated photometrically with 0.01 M 2-iodylbenzoate. The absorbance increases initially and then becomes constant after the complete reaction.