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Interaction of mercury(II) and silver(I) with bis[di(2-ethylhexyloxy)-thiophosphoryl]disulfide

Lev Bromberg[a], Isaak Lewin[b], Hugo Gottlieb[c] and Abraham Warshawsky[b,]*
[a]*Department of Materials and Interfaces and* [b]*Department of Organic Chemistry, The Weizmann Institute of Science, Rehovot 76100 (Israel)*
[c]*Department of Chemistry, Bar-Ilan University, Ramat Gan 52900 (Israel)*

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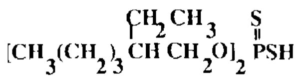
Abstract

Synthesis of bis[di(2-ethylhexyloxy)thiophosphoryl]disulfide (BTPD) by reaction of di(2-ethylhexyl)dithiophosphoric acid (DTPA) with copper(II) sulfate followed by oxidation with HNO_3 has been described. The IR spectra of BTPD have been recorded and interpreted in comparison with the spectra of DTPA on the basis of extraction experiments. Both IR and NMR spectra proved the absence of ionogenic SH groups in BTPD. The mercury and silver complexation that appeared was demonstrated to be due to redox reactions and/or insertion of metal ion or metal halide into the S–S group of BTPD. The re-extraction of metal from metal-complexed BTPD was shown to release the SH-containing components in the extractant (BTPD).

Introduction

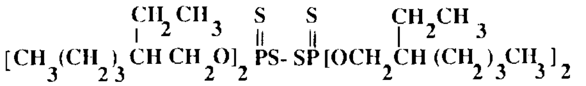
Bis[di(alkoxy)thiophosphoryl]disulfides (BTPDs) are the oxidation products of di(alkoxy)dithiophosphoric acids (DTPAs) [1, 2]. The synthesis of BTPDs usually involves oxidizing agents, such as halogens, H_2O_2, $NaNO_2$, dimethyl sulfoxide, oxygen, etc. [2, 3]. The use of BTPDs as antioxidants, lubricating oil additives [4] and reagents in organic synthesis [2] has been outlined. In comparison with the large amount of material available on the use of DTPAs for the separation of the metal ion species [1], very little is known about the metal extraction properties of BTPDs [5]. The use of odourless BTPDs may be environmentally advantageous compared to DTPAs with their strong unpleasant odour. Moreover, the solubility of BTPDs in water is much lower than that of the corresponding DTPAs [1]. These facts encourage attempts to use BTPDs in metal ion extraction.

In this paper, we have taken interest in BTPDs as novel metal complexing extractants that combine the physical properties of the parent DTPAs with a lower extraction power yet higher selectivity to mercury and silver than many other metal ions. The 2-ethylhexyloxy-substituted compound was chosen as a parent DTPA. In contrast to other DTPAs, this acid does not form stable emulsions and possesses favourable extraction kinetics [6]. The chemical formulas of the selected DTPA and BTPD are given below.



$$[CH_3(CH_2)_3\overset{\displaystyle CH_2CH_3}{\overset{|}{C}H}CH_2O]_2\overset{\displaystyle S}{\overset{\|}{P}}SH$$

DTPA



$$[CH_3(CH_2)_3\overset{\displaystyle CH_2CH_3}{\overset{|}{C}H}CH_2O]_2\overset{\displaystyle S}{\overset{\|}{P}}S\text{-}S\overset{\displaystyle S}{\overset{\|}{P}}[OCH_2\overset{\displaystyle CH_2CH_3}{\overset{|}{C}H}(CH_2)_3CH_3]_2$$

BTPD

We describe a very simple and effective procedure for the synthesis of BTPD under extraction conditions. The reagents are characterized by UV, FT-IR and NMR. The mechanism of the interaction of BTPD with Hg(II) and Ag(I) was elucidated. Furthermore, a reversible redox reaction was revealed and proven by competitive reaction using ESR.

Experimental

Reagents

Synthesis of bis[di(2-ethylhexyloxy)thiophosphoryl]-disulfide (BTPD)

2-Ethylhexanol (51.6 g, 0.4 mol) was placed in a 200-cm^3, three-necked, round-bottom flask equipped with

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*Author to whom correspondence should be addressed.

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a nitrogen inlet, a magnetic heater-stirrer, and a Liebig condenser. While the stirrer and nitrogen flow were going, the finely powdered P_2S_5 (22.2 g, 0.1 mol) (BDH Chemicals) was added slowly into the flask. The mixture was carefully heated at 70–80 °C for 2 h. The resulting precipitate was filtered off, and the organic phase dissolved in 200 cm^3 n-hexane. DTPA was converted into a sodium salt by washing with a 5 M NaOH solution (200 cm^3). The organic phase was separated, neutralized with a 2 M H_2SO_4 (200 cm^3) and washed with water (500 cm^3), and added under stirring into a mixture of KOH-saturated (20 g/dm^3) ethanol and water (200 cm^3, ratio 1:1). Ethanol solution was diluted with 200 cm^3 n-hexane and added into 200 cm^3 2 M H_2SO_4. The floating DTPA was separated, washed repeatedly with 0.25 M H_2SO_4 (500 cm^3) and water (1 dm^3), and distilled under reduced pressure to remove the hexane. The DTPA obtained has a density of 0.97 g/cm^3, and n_D^{20} 1.478.

A solution containing DTPA (36.3 g, 0.1 mol) in n-hexane (100 cm^3) was placed in a separatory funnel where an aqueous solution of copper(II) sulfate (0.07 mol, 100 cm^3) (Merck) was added. The organic and aqueous phases were carefully mixed and separated. The yellow organic phase was oxidized and decolorized by mixing with an excess of HNO_3 (5 mol, 3×300 cm^3). Then the organic phase was repeatedly washed with 0.1 M NaOH (200 cm^3) and water (3×200 cm^3), and dried under vacuum. The product was purified by flash chromatography on 40–63 μm silica gel and tested by TLC on Merck Kieselgel 60F254 plates with ethylacetate and hexane as eluants. Detection was done by UV spectroscopy or by use of 1% $KMnO_4$ in EtOH solution. The residue was an oil (29.7 g, 84% yield). *Anal.* Found: C, 54.68; H, 9.74; P, 8.56; S, 17.44. Calc. for $C_{32}P_2S_4O_4H_{68}$: C, 54.36; H, 9.68; P, 8.76; S, 18.13%.

The complexes of DTPA and BTPD as ligands with mercury and silver were prepared by solvent extraction from the corresponding aqueous solutions, using solutions of ligands in hexane or dodecane as extractants. The equilibrium extraction process was run in standard separation funnels as described previously [7, 8].

Other chemicals and solvents were of A.R. grade and were used without further purification.

Equipment and procedures

A Nicolet 510 FT-IR spectrometer was used to record all IR spectra in the range 4000–200 cm^{-1}. The IR spectra of substances in dry n-hexane were run in NaCl cells.

NMR spectra were recorded at 81 MHz on a Bruker AC200 spectrometer. The pulse angle was set to *c.* 40°. BTPD and its complexes were dissolved in $CDCl_3$. Spectra were recorded under broad-band proton decoupling; chemical shifts were referenced to external 85% H_3PO_4.

UV and visible spectra were recorded within the range 195–800 nm with a Uvikon 810 spectrophotometer in 0.1 cm quartz cells.

ESR spectra were recorded at room temperature on a Varian E-12 spectrometer in a flat cell. Spectrometer settings were: microwave power 20 mW, modulation amplitude 0.8 G, frequency 9.45 GHz, time constant 0.35 s, field 3400 G, time scale 2 min. The method to determine SH groups in BTPD developed by Weiner and co-workers [9] was used. For this determination 0.2 mM aqueous solution of bis(2,2,5,5-tetramethyl-3-imidazoline-1-oxyl-4-il)disulfide (compound $R^{\bullet}S–SR^{\bullet}$) was mixed in an equal amount of BTPD which had been obtained by re-extraction from mercury-complexed BTPD with 10 M HCl.

Results and discussion

The synthesis of BTPD from DTPA was followed by UV–Vis spectroscopy. The interaction of DTPA with copper(II) sulfate resulted in the formation of a pale yellow organic phase which had an absorption band in the visible region (420 nm). This yellowish organic phase has been found by Rudzinski and Fernando [10] to be a mixture of the copper(I) and copper(II) complexes of [dithiophosphate](dtp$^-$). The equilibria which were shown to characterize the interaction of DTPA with Cu^{2+} were described in detail in refs. 10–12. In our experiments, the ligand DTPA$^-$ was oxidized readily by nitric acid to form a colourless phase containing BTPD (eqn. (1)).

$$[S(S)PR_2]^- + NO_3^- + 2H^+ \longrightarrow \frac{1}{2}[RP(S)S\text{–}S(S)PR] + NO_2 + H_2O \quad (1)$$

Dialkyldithiphosphate ions and their oxidizing products are reversible redox systems existing on electrodes. Anions like dtp$^-$ were oxidized on dropping mercury or platinum electrodes [13, 14] or with mild oxidation agents such as iodine [2]. Extractive properties of the oxidation products of DTPA are very dependent on the method of the oxidation [12]. For example, oxidation of DTPA by a mixture of HCl and H_2O_2 led to the formation of products unable to extract mercury or silver [7]. The process of synthesis of BTPD from the cupric salt of DTPA according to eqn. (1), as well as the extraction of metals by BTPD, have not yet been described.

The IR spectra of BTPD and DTPA have an interest for us in two areas: the 1800–200 cm^{-1} region, which includes the bands typical for phosphorus–oxygen and phosphorus–sulfur vibrations, and the 2700–2400 cm^{-1} region, typical for P–SH frequencies. The high wavenumber region associated with the hydrocarbon moiety is not of interest to us. Hence we discuss the relevant absorption in the two areas. Subsequently, we have discovered (see further discussion) that BTPD undergoes chemical changes during the extraction process.

The assignments of the absorption bands in the 1800–200 cm^{-1} region are consistent with the following: very intense bands at 1049–964 cm^{-1} arise from (P)–O–C stretching modes; strong absorption bands arise from P–O(C) stretching modes at 875–730 cm^{-1}; bands of variable intensity arise at 1240–1080 cm^{-1} from deformations involving the carbon atom [15]. Both P=S and P–S antisymmetric and symmetric stretching frequencies are found at 667, 659 and 528 cm^{-1}, respectively, in accordance with the typical P=S and P–S stretching frequencies [2]. The band at 386 cm^{-1} is assigned to the O–P–O band superimposed on the PS and SPS stretches, as also observed by Rudzinski *et al.* [15].

Another important region in which (P)–S–H valent frequencies were found in a study of DTPA and its metal ion complexes is 2600–2400 cm^{-1} [6]. The band at 2603 cm^{-1} with a smooth shoulder in the spectrum of BTPD, as well as the band at 2593 cm^{-1} with a shoulder at 2567 cm^{-1} and the band at 2463 cm^{-1} with a shoulder at 2479 cm^{-1} in the spectrum of DTPA were observed (Fig. 1). But the 'responses' of the IR spectra to the saturation of BTPD and DTPA by Ag$^+$ ions were completely different. Saturation was carried out by extraction. There was no change in the spectrum of BTPD, but the spectrum of DTPA changed noticeably. The band at 2593 cm^{-1} split into two bands of lower intensity at 2605 and 2587 cm^{-1} (Fig. 1, B). The band at 2460 cm^{-1} disappeared. These experiments allow one to assign the broad band at 2603 cm^{-1} in the spectrum of BTPD (Fig. 1, C) to the C–H stretches associated with the methyl moiety [15] rather than the S–H groups. The absence of SH-containing components in uncomplexed BTPD was proven by NMR. The ^{1}H NMR spectra of BTPD and DTPA revealed the presence of S–H groups in DTPA (band at 4.30 ppm), then their disappearance after the saturation with silver ions, and the absence of S–H groups in the spectrum of BTPD.

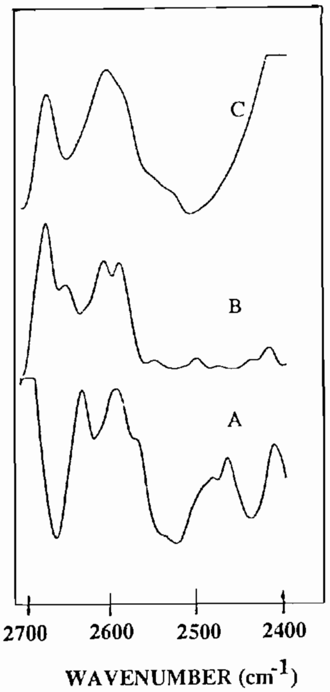

Fig. 1. FT-IR spectra of DTPA (A), silver-complexed DTPA (B) and BTPD (C) within the range 2700–2400 cm^{-1}.

It has been proven that the bands found in the 400–200 cm^{-1} region of the IR spectra are mainly due to metal–S stretches [15, 16]. These frequences are fairly dependent on the nature of the metal [17]. Spectra of BTPD complexed with mercury(I), mercury(II), and silver(I) are shown in Fig. 2, A, B and C, respectively. It can be seen that the band at 386 cm^{-1} is nearly absent in the spectrum of the fresh mercury(I)-complexed BTPD (Fig. 2, A). This band can be assigned to SPS and PS symmetric stretching frequencies [15]. After 3 days in the solvent, this spectrum changed and was shown to be very similar to the spectrum of the mercury(II)-complexed BTPD with an intense band

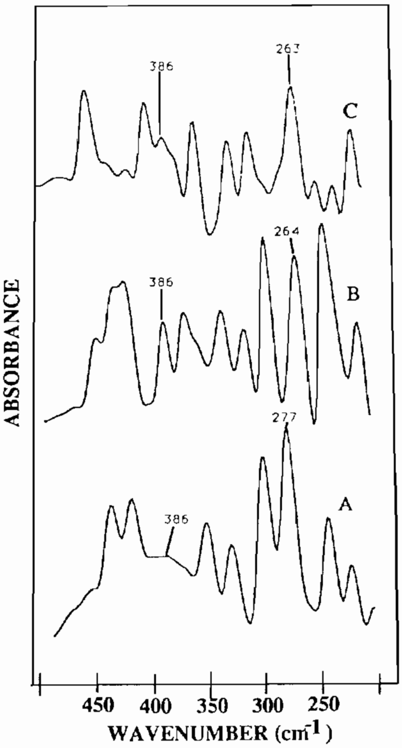

Fig. 2. FT-IR spectra of BTPD complexed with mercury(I) (A), mercury(II) (B) and silver (C).

shifted to 386 cm^{-1} (Fig. 2, B). This is probably due to redox reactions (eqns. (2)–(4)) in the complexation process [1, 10].

$$\frac{1}{2}[RP(S)S\text{–}S(S)PR] + e^- \longrightarrow [RP(S)S]^- \qquad (2)$$

$$Hg^+ - e^- \longrightarrow Hg^{2+} \qquad (3)$$

$$2[RP(S)S]^- + Hg^{2+} \longrightarrow [RP(S)S]_2Hg \qquad (4)$$

The bands at 277, 264 and 263 cm^{-1} in the spectra of Hg(I), Hg(II) and Ag-complexed BTPD, respectively (Fig. 2) were absent in the spectrum of pure BTPD. The metal ion complexation shifts the bands at 249, 289, 310 and 334 cm^{-1} in the spectrum of BTPD to the stretching frequencies shown in Table 1.

These data correlate quite well with the ones found in refs. 16 and 17. In a study of mercury-complexed bis[di(ethyl)thiophosphate] Adams and Cornell [17] found the Hg–S stretching frequency at 280 and 239 cm^{-1}. Wasson *et al.* [16] gave a review of the data concerning metal–S stretches which had been assigned to metal–dithiophosphate complexes. Metal–sulfur stretching frequency correlations in the region 400–200 cm^{-1} have been discussed [18].

A comparison of the IR spectra of both uncomplexed and metal-complexed BTPD (Fig. 2) showed that the S–S bond in BTPD could be partially inserted giving a metal–dithiophosphate complex [2]. Such observations were made by Muratova *et al.* [19] who reported an insertion of tin dihalides in the S–S bond of bis[di(alkoxy)thiophosphoryl]disulfide according to the following scheme (eqn. (5)).

$$[R'_2P(S)S]_2 + SnX_2 \longrightarrow [R'_2P(S)S]_2SnX_2 \longrightarrow R'_2P(S)\text{-}S\text{-}(X)Sn(X)\text{-}S(S)PR'_2 \qquad (5)$$

where X = halide, R'_2 = iso-C_3H_7O

Hu and Chen [20] demonstrated the formation of products like $[R''_2P(S)S]_2HgCl_2$, $[R''_2P(S)S]_2Hg$ and $[R''_2P(S)S]_2S_3$ as a result of reaction of disulfide with $HgCl_2$ (R″ = EtO).

The interaction of BTPD with mercury or silver could also be followed by ^{31}P NMR. The ^{31}P spectrum of BTPD shows a major peak at 86.86 ppm and a small peak at 79.99 ppm (ratio of intensities is 0.10). (This peak may be due to a copper complex formed in the solution of BTPD.) Upon complexation with mercury chloride the 79.99 ppm peak increased, and the ratio of intensities of the peaks at 79.99 and 86.86 ppm for $HgCl_2$-complexed BTPD reached 0.61.

TABLE 1. The main shifts observed in the IR spectra of BTPD-complexed metal ions

Pure BTPD	Complexed ion		
	Hg^+	Hg^{2+}	Ag^+
Wavenumber (cm^{-1})			
249	242	240	245
289	298	291	304
310	328	312	321
334	350	365	352

The hypothesis that metal interaction during complexation in solution leads to the appearance of a free SH group was examined by an ESR experiment in the presence of a disulfide probe (compound R˙S–SR˙) which readily equilibrates with SH-containing compounds according to the metathesis reaction (6) [9]

$$BTPD\text{–}SH + R^{\cdot}S\text{–}SR^{\cdot} \rightleftharpoons R^{\cdot}\text{–}SH + BTPD\text{–}S\text{–}SR^{\cdot} \qquad (6)$$

In our case R˙–SH could be a free SH form of BTPD or most probably even DTPA itself. The signal of the free monoradical R˙–SH is represented by the intensity of feature 1 and correlated to the signal of the biradical R˙S–SR˙ (feature 2, Fig. 3). To avoid misconception, control experiments with $HgCl_2$ and R˙S–SR˙ were carried out, showing no effect on ESR spectra of the compound R˙S–SR˙, itself.

These data suggest that re-extraction of metal from metal-complexed BTPD leads to the appearance of SH groups in the extractant due to the possible breakdown of the S–S bond during the extraction through the insertion of Hg^{2+} or $HgCl_2$ (eqn. (7)).

$$RP(S)\text{–}S\text{–}Hg\text{–}S\text{–}(S)PR + 2HCl \rightleftharpoons 2RP(S)\text{–}SH + HgCl_2 \qquad (7)$$

In fact, after the re-extraction of mercury or silver from the complexes by concentrated HCl, BTPD did

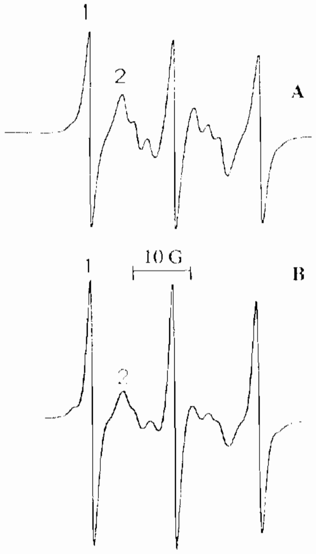

Fig. 3. ESR spectra of 2×10^{-4} M R˙S–SR˙ biradical solution (A) and of the mixture of 2×10^{-4} M R˙S–SR˙ biradical and 2×10^{-4} M BTPD (B). Gain 2×10^2 (A) and 8×10^3 (B).

contain SH groups, as its ^{1}H NMR spectrum after re-extraction was similar to the spectrum of DTPA. The changes in the ESR spectra of BTPD, obtained by re-extraction from BTPD-complexed $HgCl_2$, provide further evidence of the breakdown of the S–S bond due to interaction with mercury (Fig. 3).

This was further substantiated by the ability of DTPA, obtained after the re-extraction of mercury from the mercury–BTPD complex, to partially react with copper(II) sulfate, giving the coloured copper(II)–DTPA$^-$ complex.

Hence, the conclusions are that the extraction of mercury or silver by BTPD led to the breakdown of the S–S bond and/or to the insertion of ion or metal halide into it. Next, re-extraction of metal from the metal–BTPD complex produces some SH-containing components in BTPD which showed capacity to react with Cu(II). The SH-containing components could be changed back into disulfide (BTPD) by reaction with copper ions.

Acknowledgements

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