TABLE I

COULOMETRIC n-VALUES FOR THE REDUCTION OF Ru(IV) IN 4 M KCl (pH 1.5)

Applied potential = −0.470 v. *vs.* s.c.e.

Ruthenium(IV), mmoles	mfaradays consumed	n
0.171	0.346	2.02
.168	.337	2.01
.172	.342	1.99
		Mean 2.01 ± 0.01

were of reagent grade. Cathode potentials were controlled by means of a Model 600 electronic potentiostat (Duffers Associates, Inc., Troy, N. Y.). Electrolyses were carried out in a cell providing a mercury pool cathode of 184 cm.^{2} area and a platinum gauze anode separated from the cathode compartment by a "fine" fritted glass disk. A Leeds and Northrup saturated calomel electrode served as a reference. The catholyte was continuously purged with N_2 during electolysis and kept at 25 ± 0.2°. Spectra were recorded with a Beckman DB UV-visible spectrophotometer.

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CONTRIBUTION FROM THE
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The Oxidation of O,O-Diethyl Hydrogen Dithiophosphate and its Polysulfides

BY GERSHON METZGER

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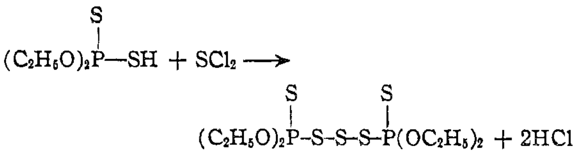
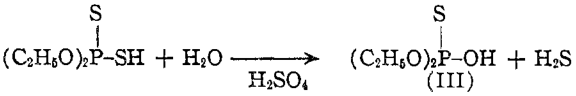
It has been reported[1] that oxidation of O,O-diethyl hydrogen dithiophosphate with concentrated sulfuric acid results in the formation of bis-(diethoxythiophosphoryl) disulfide, $(C_2H_5O)_2\overset{S}{P}\text{-S-S-}\overset{S}{P}(OC_2H_5)_2$ (I). Re-investigation of this reaction has shown that the reaction product is actually a mixture of (I) and bis-(diethoxythiophosphoryl) trisulfide,[2] $(C_2H_5O)_2\overset{S}{P}\text{-S-S-S-}\overset{S}{P}(OC_2H_5)_2$ (II). The identity of the latter was confirmed by a mixed melting point determination (m.p. 72–73°) with an authentic sample prepared by the reaction


$$(C_2H_5O)_2\overset{S}{P}\text{—SH} + SCl_2 \longrightarrow (C_2H_5O)_2\overset{S}{P}\text{-S-S-S-}\overset{S}{P}(OC_2H_5)_2 + 2HCl$$

Compound I can originate *via* a straightforward oxidation of O,O-diethyl hydrogen dithiophosphate or one of its metal salts. In fact, a large variety of other oxidizing agents generate (I) as well, *e.g.*, Cl_2,[3,4] I_3^-,[5] HNO_2,[5] H_2O_2,[3] etc. The formation of compound II, however, is complicated by some mechanism that makes an extra sulfur atom available during the oxidation of the free acid.

The oxidation of O,O-diethyl hydrogen dithiophosphate with either iodine or H_2O_2 results in a quantitative yield of (I). When Na_2S (an obvious source of sulfur) is added to the iodine oxidation, or when the H_2O_2 oxidation is carried out in strongly acidic media, some of (II) is obtained as well. This suggests that the extra sulfur required in the H_2SO_4 oxidation process may result from hydrolysis and subsequent oxidation of the H_2S produced by hydrolysis


$$(C_2H_5O)_2\overset{S}{P}\text{-SH} + H_2O \xrightarrow[H_2SO_4]{} \underset{\text{(III)}}{(C_2H_5O)_2\overset{S}{P}\text{-OH}} + H_2S$$

Compound III has been isolated and identified. Its potassium salt was prepared and the melting point, 195–197°, is in excellent agreement with the literature value[6] of 196–197°. The amount of compound III obtained was approximately equivalent to the amount of compound II found. These observations are consistent with the above mechanism if (III) is stable to further hydrolysis even in strongly acidic media.

It thus has been demonstrated that the straightforward oxidation of O,O-diethyl hydrogen dithiophosphate to its disulfide can be modified so that some trisulfide is produced as well. The modification consists essentially of making reactive elemental sulfur available during the course of the reaction.

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[1] B. L. Johnson, U. S. Patent No. 1,763,851 and 1,763,852.

[2] The identification of this material as a product of the reaction was originally noted by J. A. Price of Esso Research and Engineering Co., Linden, New Jersey.

[3] L. Malatesta and F. Laverone, *Gazz. chim. ital.*, **81**, 596 (1951).

[4] T. Gamasaki, *Sci. Repts. Res. Inst., Tohoku Univ.*, **A4**, 403 (1952).

[5] M. I. Kabachnik and T. A. Mastryukova, *Izv. Akad. Nauk SSSR Otd. Khim. Nauk*, 121 (1953).

[6] T. W. Masters, G. R. Norman, and E. A. Weilmuenster, *J. Am. Chem. Soc.*, **67**, 1662 (1945).

Experimental

The Preparations of O,O-Diethyl Hydrogen Dithiophosphate, Bis-(diethoxythiophosphoryl) Disulfide, and Bis-(diethoxythiophosphoryl) Trisulfide.—These compounds were prepared by reported procedures.[3,7]

The Oxidation of O,O-Diethyl Hydrogen Dithiophosphate by Concentrated Sulfuric Acid.—$(C_2H_5O)_2P(S)SH$ (30 g.) was added slowly to concentrated H_2SO_4 (25 g.) with vigorous stirring and cooling in an ice bath. The addition took approximately 1 hr., then an additional 10-g. sample of H_2SO_4 was added to the reaction mixture. The ice bath was removed and the reaction mixture was stirred overnight. The mixture was diluted with 120 ml. of H_2O and then was extracted with three 66-ml. aliquots of aqueous NaOH (4%). The ether extract was dried over Na_2SO_4 and then blown free of solvent with N_2 gas on the steam bath. Cooling the residual oil resulted in the crystallization of a 3.82-g. sample of bis-(diethoxythiophosphoryl) trisulfide which was isolated by filtration (27% yield based on P), m.p. 72°. *Anal.* Calcd. for $C_8H_{20}O_4P_2S_5$: C, 23.9; H, 5.0; P, 15.4; S, 39.8. Found: C, 23.3; H, 4.9; P, 15.5; S, 40.0. The filtrate, weighing 14.6 g., had an infrared spectrum identical with that of an authentically prepared sample of bis-(diethylthiophosphoryl) disulfide (49% yield based on P). *Anal.* Calcd. for $C_8H_{20}O_4P_2S_4$: C, 25.9; H, 5.4; P, 16.7; S, 34.6. Found: C, 25.1; H, 5.2; P, 16.3; S, 34.2. This material was readily converted into the trisulfide (identified by mixed melting point determination) upon being heated with excess sulfur. The conversion was catalyzed by a few per cent of added P_2S_5.

The combined aqueous NaOH extracts were acidified with concentrated HCl. An additional 5-ml. sample of HCl was added and the resultant solution extracted with three 50-ml. aliquots of ethyl ether. The ether extracts were dried over Na_2SO_4 and blown free of solvent with N_2 gas on a steam bath. A 3-g. sample of $(C_2H_5O)_2P(S)OH$ was obtained (11% yield based on P). *Anal.* Calcd. for $C_4H_{11}O_3PS$: C, 28.2; H, 6.5; P, 18.2; S, 18.8; neut. equiv., 170. Found: C, 28.5; H, 6.8; P, 18.3; S, 19.0; neut. equiv., 169. The melting point of the potassium salt, 195–197°, was in excellent agreement with the literature value of 196–197°.[7]

The Modified Oxidation of O,O-Diethyl Hydrogen Dithiophosphate with Iodine.—To a mixture of $(C_2H_5O)_2P(S)SH$ (9.3 g.), H_2O (100 ml.), and 3 *N* KOH (17 ml.) were added simultaneously and with vigorous stirring 0.5 *N* Na_2S (100 ml.) and 0.1 *N* KI–I_2 solution (1000 ml.). The addition took approximately 20 min. and the resultant mixture was stirred for an additional 1 hr. At the end of this time, the reaction mixture was extracted with five 200-ml. portions of benzene. The combined benzene extracts were washed with two 100-ml. portions of 3 *N* KOH and with 100 ml. of H_2O. The benzene solution was dried over Na_2SO_4 and then blown free of solvent on a steam bath under a stream of N_2 gas; 1.8 g. of bis-(diethoxythiophosphoryl) trisulfide (18% yield) and 7.7 g. of the disulfide (83% yield) remained.

The Hydrogen Peroxide Oxidation of O,O-Diethyl Hydrogen Dithiophosphate in Concentrated Acid Medium.—To 180 ml. of concentrated HCl were added successively 18.6 g. of $(C_2H_5O)_2P(S)SH$ and 11.5 cc. of 30% H_2O_2 solution. The latter was added dropwise with vigorous stirring over a period of 2 hr. at a temperature of 25–30°. The reaction mixture was extracted with three 50-ml. aliquots of benzene. The extracts were washed with dilute sodium hydroxide followed by distilled water and the solvent was removed as before. Bis-(diethoxythiophosphoryl) trisulfide (2.5 g., 12% yield) and 11.5 g. of the disulfide (62% yield) remained.

CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC
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Formation Constants of the Complex Species Formed by Interaction of Rare Earth N′-Hydroxyethylethylenediamine-N,N,N′-triacetate Complexes with an Equivalent Amount of Base[1]

BY ASIM K. GUPTA AND JACK E. POWELL

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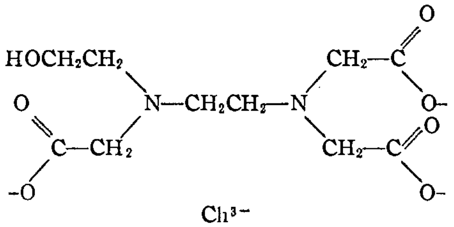
From the pH buffering properties and solubility of rare earth N′-hydroxyethylethylenediamine-N,N,N′-triacetate (HEDTA) complexes in base, it has been assumed tentatively that sparingly soluble, neutral, RCh species combine with an equivalent amount of base to form new complex species of the type $RChOH^-$. That is, at constant ionic strength



Ch^{3-}

$$K'_{\mathrm{RChOH}} = \frac{[\mathrm{RChOH}^-]}{[\mathrm{RCh}][\mathrm{OH}^-]} \qquad (1)$$

is a constant. Whether the reaction mechanism is regarded as the substitution of a hydroxyl ion for a molecule of coördinated water, as the displacement of the coördinated hydroxyethyl donor group of HEDTA by OH^-, or merely as the loss of a proton by a coördinated entity (either a coördinated water molecule or the hydroxyethyl group) is immaterial.

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(7) H. Rudel and J. M. Boyle, U. S. Patent No. 2,523,146.

(1) Contribution No. 1111. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.