[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

Some Trialkyl Trithio-phosphorus, Antimony and Bismuth Compounds

BY ARNOLD LIPPERT AND E. EMMET REID

In 1872 Michaelis[1] reported triethyl trithiophosphite as a heavy oil boiling at 240–280° with sp. gr. 1.24 at 12°. Claesson[2] and Klason[3] described the triethyl trithio-phosphite, arsenite and antimonite and bismuth mercaptide. As the data on these compounds are incomplete it seemed desirable to prepare them again along with several propyl and butyl compounds for comparisons among themselves and with the corresponding oxygen compounds.

It was found that a trithiophosphite can be obtained by refluxing a mercaptan with phosphorus trichloride but that the corresponding reactions with arsenic and antimony stop at the monochloro stage. Following the method for preparing alkyl phosphites[4] pyridine (3 moles) was added to the mixture of mercaptan and phosphorus trichloride. Fair yields were thus obtained but the results were much better (up to 70% yields) with dimethylaniline. This method is satisfactory for the trithioarsenites and trithioantimonites.

The trialkyl trithiophosphites are colorless oils with characteristic and powerful odors, insoluble in water but readily soluble in the usual organic solvents and in concd. sulfuric acid. They are stable in the presence of water, concd. hydrochloric acid or dry hydrogen chloride but are readily hydrolyzed by alkalies. Unlike their oxygen analogs they decompose when heated in air to 90°. They are oxidized by 3% hydrogen peroxide and acetic acid to the trithiophosphates, while stronger oxidizing agents such as 60% hydrogen peroxide, nitric acid and acid permanganate or chromate break them down into phosphoric acid and alkyl sulfonic acids. Chlorine and bromine react with them to give alkyl disulfides and phosphoric acid but one mole of the triethyl ester takes up exactly two atoms of iodine from an alcoholic solution. This addition product was poured into water from which, after several weeks, large transparent hydrated crystals separated. These were soluble in water and sublimed at a high temperature without residue.

The trialkyl trithiophosphites combine with methyl iodide, in several weeks of standing, to give colorless needles; in alcohol or ether solution they react at once with mercuric bromide or iodide or auric chloride to give addition products which have definite melting points. The compounds with mercuric bromide are colorless needles while the others are yellow. More or less unstable addition compounds are formed with mercuric chloride, silver nitrate, lead nitrate and cuprous chloride but none with ammonia, ferric chloride, cupric chloride or pyridine. They reduce alcoholic ferric chloride. Attempts to add sulfur to form the thiophosphates were unsuccessful due to the unstability of the esters when heated above 90°.

Triethyl trithioantimonite was prepared similarly with the aid of dimethylaniline but the yield (30%) was not so good as that with the corresponding phosphorus compounds. A better yield was obtained by using sodium mercaptide. Klason[3] reports making it by the action of antimony trichloride in strong aqueous hydrochloric acid on mercaptan. We were unable to obtain it in this way. The ester is a viscous light yellow oil insoluble in water. On contact with air it decomposes into ethyl disulfide and antimony trioxide. When sealed in glass capsules it slowly turned green with the deposition of metallic antimony. This seemed to be catalyzed by previous exposure to air. In solution in dry ether the ester was stable. It burns with a bright, slightly smoky flame. Addition of iodine to an alcoholic solution gave a pale yellow unstable addition product.

The properties of these esters and their addition compounds are shown in Table I.

The triethyl bismuth mercaptide was formed by the addition of bismuth nitrate crystals to mercaptan. Reaction takes place immediately with the formation of an aqueous layer and a red solution which when poured into ether precipitated the mercaptide as a yellow powder, melting at 200° with decomposition agreeing with the observations of Claesson.

Experimental

To a chloroform solution of 25 g. of ethyl mercaptan in a flask with reflux condenser and mercury-seal stirrer, kept at 0°, 13.7 g. of phosphorus chloride was added slowly with

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(1) Michaelis, *Ber.*, **5**, 7 (1872).

(2) Claesson, *Bull. soc. chim.*, [2] **25**, 183 (1876); *J. prakt. Chem.*, [2] **15**, 209 (1877).

(3) Klason, *Acta Univ. Lund.*, **21**, 3 Abt. Abl. VI, p. 14 (1884–1885).

(4) Milobendzki and Sachnowski, *Chemik Polski*, **15**, 34 (1917); *J. Chem. Soc.*, **114**, i, 477 (1918).

TABLE I

THE TRIALKYL TRITHIOPHOSPHITES AND ANTIMONITE AND THEIR ADDITION COMPOUNDS

							M. p.'s add. comps. with			
Formula	B. p., °C.	Press.	M. p., °C.	n^{25}_D	d^0_4	d^{25}_4	CH_3I	$HgBr_2$	HgI_2	$AuCl_3$
$(EtS)_3P$	140–143	18	− 32–31	1.5689	1.1883[a]	1.1585	191	184	187	225
$(PrS)_3P$	164–169	15	− 65–64	1.5350	1.1277	1.0932	191	176	182	208
$(BuS)_3P$	174–180	15	−101–100	1.5305	1.0773	1.0421	198	148	162	182
$(EtS)_3PO$[b]	165–168	15	− 24–23	....	....	1.1890				
$(EtS)_3Sb$	167–170	4	....	....	1.6224	1.5873				

[a] Claisson gives sp. g. at 12° 1.24. [b] Pischtschimuka gives b. p. 174–175 (20 mm.) d^0_0 1.1969.

stirring which was continued for an hour after all was in. The product was heated to 70° at atmospheric pressure and the residue distilled at 18 mm., yield 7.5 g. or 35%. To a solution of 18.6 g. of mercaptan and 24 g. of dimethylaniline in 100 cc. of ether, 13.7 g. of phosphorus trichloride was added under the same conditions. The dimethylaniline hydrochloride was filtered off and extracted with ether. The ether solution was treated as above, yield 13.3 g. or 62%. Using 10% excess of mercaptan brought the yield to 70%. *Anal.* Calcd.: P, 14.48; S, 44.86. Found: P, 14.58; S, 44.31.

The tripropyl ester was prepared similarly, yield 58%. *Anal.* Calcd.: P, 12.11; S, 37.50. Found: P, 12.25; S, 37.43.

Similarly the tributyl ester was obtained in 58% yield. *Anal.* Calcd.: P, 10.40; S, 32.21. Found: P, 10.41; S, 31.86.

To a solution of 10 g. of the triethyl ester in 200 cc. of acetic acid, 50 cc. of 3% hydrogen peroxide was added and the mixture stirred for twelve hours. The acid was neutralized with ammonia and the oil extracted with ether and distilled, b. p. 165–170° at 15–18 mm., yield 34%.

An ether solution of antimony trichloride was added with rapid stirring and efficient cooling to sodium ethyl mercaptide in a flask with reflux. Reaction took place immediately but the mixture was stirred for six hours, after which the salt was filtered off and the solution distilled. The yield of ester was 80%, analysis Sb found 39.48%, calculated 39.60%.

Summary

Triethyl, tripropyl and tributyl trithiophosphites, triethyl trithioantimonite and bismuth triethyl mercaptide have been prepared and their properties determined. The trithiophosphites form many addition products.

BALTIMORE, MARYLAND RECEIVED JULY 11, 1938

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

The Conductance of Hydrochloric Acid in Dioxane–Water Mixtures from 15 to 45°

BY BENTON BROOKS OWEN AND GEORGE W. WATERS[1]

The effects of viscosity, temperature and dielectric constant upon the conductivity of solutions of electrolytes have long been popular subjects for investigation. In view of the peculiar conductance mechanism of the hydrogen ion, it is surprising that such a small part of this work has dealt with solutions of acids. Goldschmidt[2] and his co-workers have measured the conductance of several acids at 25° in alcohol–water mixtures rich in alcohol, and a number of investigators[3] have studied acids in pure non-aqueous solvents, for the most part at 25°. In the present research, we have measured the conductance of hydrochloric acid in four dioxane–water mixtures, 20, 45, 70 and 82% dioxane by weight, at 15, 25, 35 and 45°. By subjecting this important electrolyte to considerable variation in both dielectric constant and temperature, we not only extend our knowledge of the effects of these variables upon conductance, but also derive some information regarding its thermodynamic properties. This thermodynamic information is of immediate interest, because it supplements the extensive electrochemical investigation of hydrochloric acid in dioxane–water mixtures by Harned[4] and his students.

Materials, Technique and Fundamental Constants

Conductivity water was distilled from alkaline permanganate in an electrically heated Barnstead still. The dioxane was obtained from the Carbide and Carbon Chemi-

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(1) This communication embodies part of the thesis presented by George W. Waters to the Graduate School of Yale University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) Goldschmidt, *Z. physik. Chem.*, **89**, 129 (1914); **91**, 46 (1916); **91**, 51 (1916); **70**, 633 (1910).

(3) For bibliography consult the review by Hartley, Gatty, MacFarlane and Murray-Rust, *Ann. Repts. Chem. Soc.* (London), **27**, 326 (1931).

(4) Harned and Morrison, *Am. J. Sci.*, **33**, 161 (1937); THIS JOURNAL, **58**, 1908 (1936); Harned, *ibid.*, **60**, 336 (1938); Harned and Donelson, *ibid.*, **60**, 339 (1938); **60**, 2128 (1938); Harned and Calmon, *ibid.*, **60**, 2130 (1938); Harned, Donelson and Calmon, *ibid.*, **60**, 2133 (1938).