supports this hypothesis is derived from measurements of the conductivity of solutions of stannic chloride in alcohol. Wertyporoch and Altmann[11] measured the specific conductivities of solutions of stannic chloride in alcohol at 0°. Values of 2.53, 2.88 and 3.83 × 10^{-4} ohms^{-1} were obtained for stannic chloride concentrations of 0.0436, 0.0863 and 0.1293 mole per liter, respectively. According to Smyth,[12] the tin–chlorine bond in stannic chloride is almost electrovalent in character. According to Delwaulle and Francois,[13] and Prytz,[14] stannous chloride and chloride ion, in aqueous solutions, react to form the complex ion $SnCl_3^-$. It is assumed that this reaction would also take place in alcohol solutions.

Acknowledgment.—The authors wish to express their appreciation to Dr. R. W. Spence and Mr. James Sattizahn of the Los Alamos Scientific Laboratory for irradiation of the samples of stannic chloride.

[11] E. Wertyporoch and B. Altmann, *Z. physik. Chem.*, **A168**, 1 (1934).

[12] C. P. Smyth, THIS JOURNAL, **60**, 183 (1938).

[13] M. L. Delwaulle and F. Francois, *Compt. rend.*, **211**, 65 (1940).

[14] M. Prytz, *Z. anorg. allgem. Chem.*, **172**, 147 (1928).

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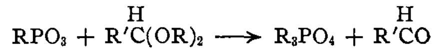
[CONTRIBUTION FROM THE PROCESS IMPROVEMENT AND DEVELOPMENT LABORATORIES, TENNESSEE EASTMAN COMPANY]

Reactions of Some Orthoesters with Phosphorus Pentoxide and Phosphorus Pentasulfide

BY KENT C. BRANNOCK*

The reactions of some aliphatic orthoesters with phosphorus pentoxide and phosphorus pentasulfide have been investigated. Ethyl orthoformate and phosphorus pentoxide yield triethyl phosphate, tetraethyl pyrophosphate and ethyl formate. Phosphorus pentasulfide and ethyl orthoformate react to give a triethyl dithiophosphate, ethyl formate and ethyl thionoformate. Phosphorus pentasulfide and ethyl orthothioformate give triethyl tetrathiophosphate and ethyl dithioformate, while under similar conditions phosphorus pentoxide and ethyl orthothioformate do not react. The scope and limitations of this type of reaction remain to be determined.

The preparation of trialkyl phosphates by the interaction of an alkyl metaphosphate and an acetal has been reported.[1] This may be illustrated as follows[2]



$$RPO_3 + R'\overset{H}{C}(OR)_2 \longrightarrow R_3PO_4 + R'\overset{H}{C}O$$

In view of this reaction, it seemed logical to investigate the reactions of the acetal-like alkyl orthoesters with compounds having a polyphosphate structure, such as phosphorus pentoxide. A literature survey disclosed that Staudinger and Rathsam[3] attempted to obtain ketene acetal by treating ethyl orthoformate with phosphorus pentoxide, but obtained ethyl formate instead. Similar results were obtained with ethyl orthoacetate and ethyl orthopropionate, and the reaction was thought to proceed as $RC(OEt)_3 \xrightarrow{P_2O_5} RCOOEt + Et_2O$. Although no ether was obtained, they speculated that it was formed but underwent further reaction with the phosphorus pentoxide. Under the conditions used by these authors any ether formed in the reaction should have been recovered, since the reaction of ether with phosphorus pentoxide at temperatures attainable under atmospheric pressure is very slow. For example, the preparation of ethyl metaphosphate from phosphorus pentoxide and excess ether at reflux temperature requires about 60 hours.[4]

It has been shown in the present investigation that ethyl orthoformate reacts with phosphorus pentoxide at elevated temperatures to give triethyl phosphate, tetraethyl pyrophosphate and ethyl formate. The over-all reactions may be illustrated by the equations

$$P_2O_5 + 2HC(OEt)_3 \longrightarrow 2HCOOEt + (EtO)_2P(O)OP(O)(OEt)_2$$

$$P_2O_5 + 3HC(OEt)_3 \longrightarrow 3HCOOEt + 2Et_3PO_4$$

Extending the reaction to the sulfur analogs, it was found that ethyl orthoformate and phosphorus pentasulfide at 95–150° give ethyl formate, ethyl thionoformate and a triethyl dithiophosphate. No chemical evidence was obtained to justify the assignment of a definite structure to the latter compound; therefore, it may be either O,O,S-triethyl dithiophosphate or O,S,S-triethyl dithiophosphate.

$$P_2S_5 + 3HC(OEt)_3 \longrightarrow 2HCOOEt + HCSOEt + 2Et_3PO_2S_2$$

Similarly, ethyl orthothioformate and phosphorus pentasulfide give triethyl tetrathiophosphate and, by analogy, ethyl dithioformate.

$$P_2S_5 + 3HC(SEt)_3 \longrightarrow 3HCSSEt + Et_3PS_4$$

Ethyl orthothioformate and phosphorus pentoxide do not appear to react at 150°.

The mechanism of this type of reaction as well as its scope and limitation remains to be determined.

Acknowledgment.—The author is indebted to Mr. Stanley A. Murray of these laboratories for his helpful discussions and the tetraethyl pyrophosphate analysis reported below.

Experimental[5]

Materials.—The phosphorus pentoxide and phosphorus pentasulfide used in this investigation were commercial products. Ethyl orthoformate was a redistilled Eastman

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[1] D. C. Hull and A. H. Agett, U. S. Patent 2,430,569 (1947).

[2] For the sake of simplicity the empirical formula of the alkyl metaphosphate is used, although it is known that these esters exist in a condensed or polyphosphate state. This is discussed briefly in G. M. Kosolapoff, "Organophosphorus Compounds," Chapter 12, John Wiley and Sons, Inc., New York, N. Y., 1950.

[3] H. Staudinger and H. Rathsam, *Helv. Chim. Acta*, **5**, 645 (1922).

[4] K. Langheld, *Ber.*, **44**, 2076 (1911).

[5] All boiling points are uncorrected.

Kodak product. Ethyl orthothioformate was prepared from ethyl formate and ethyl mercaptan by the method of Holmberg.[6]

Phosphorus Pentoxide and Ethyl Orthoformate.—Thirty-seven grams of phosphorus pentoxide (0.26 mole) was added as rapidly as possible to 275.5 g. of ethyl orthoformate (1.81 moles). The mixture was heated with agitation to 125° over a 3.5-hour period and maintained at 125° for an additional 3.5 hours. During this time 28 g. of ethyl formate was distilled from the reaction mixture through a side-arm and condensed. Vacuum distillation of the reaction mixture gave 186 g. of ethyl orthoformate, b.p. 41–43° at 10–11 mm.; 10.4 g. of triethyl phosphate, b.p. 52° at 1 mm.; and 37.5 g. of impure tetraethyl pyrophosphate, b.p. 125–130° at 0.4–0.5 mm. During the vacuum distillation an additional 12.2 g. of ethyl formate was collected in the Dry Ice trap. Ethyl formate was identified by boiling point and saponification equivalent.

Anal. Triethyl phosphate. Calcd. for $C_6H_{15}O_4P$: P, 17.01. Found: P, 16.89. Tetraethyl pyrophosphate. Analysis[7] showed 76.0% tetraethyl pyrophosphate and 22.5% triethyl phosphate. Calcd. for this mixture: P, 20.06. Found: P, 19.95.

Phosphorus Pentasulfide and Ethyl Orthoformate.—One hundred and thirty-four grams of ethyl orthoformate (0.905 mole) and 61 g. of phosphorus pentasulfide (0.275 mole) were combined in a 500-cc. flask and heated over a 15-minute period to 95°. At this temperature an exothermic reaction began and the heat source was removed. After 15 minutes the reaction had subsided and heating was resumed. The temperature was raised to 150° over the next 30 minutes. During this time 56.5 g. of ethyl formate and ethyl thionoformate was distilled from the reaction mixture and condensed. The reaction mixture was then distilled under vacuum. At 10 mm. pressure 12.3 g. of ethyl formate and ethyl thionoformate was collected in the Dry Ice trap and 5.5 g. of ethyl orthoformate distilled at 40–42°. The pressure was then reduced to 0.65 mm. and 109.2 g. (92.5%) of crude triethyl dithiophosphate was collected at 66–74°. Redistillation of the crude phosphate gave 94 g. of the pure compound boiling sharply at 115–115.5° at 10 mm.[8]; $n^{20}D$ 1.5010.

The ethyl formate–ethyl thionoformate fractions were combined and fractionated under nitrogen to give 39.2 g. (96%) of ethyl formate at 53–54°, an intermediate fraction of 2 g. from 54–86°, and 15.5 g. (63%) of ethyl thionoformate from 86–89°. The 86–89° fraction was yellow in color, had a strong ozone-like odor, and on saponification gave no ethyl mercaptan. On acidification the solution from the saponification liberated hydrogen sulfide. A 1.1390-g. sample used 22.1 ml. of *N* NaOH, corresponding to 87.5% ethyl thionoformate based on the expected hydrolysis: $HCSOEt + H_2O \rightarrow HCOOH + H_2S$. It is probable that some oxidation of the thiono sulfur took place on exposure of the sample to air during the saponification.

Anal. Triethyl dithiophosphate. Calcd. for $C_6H_{15}O_2S_2P$: S, 29.93; P, 14.46. Found: S, 30.03; P, 14.44.

Saponification for 6 hours with alcoholic potassium hydroxide gave a saponification equivalent of 214. The theoretical if one alkyl group is removed is 214. Saponification for 18 hours with aqueous sodium hydroxide gave a saponification equivalent of 217.9. There was no indication of loss of sulfur as sulfide in either saponification.

Anal. Ethyl thionoformate. Calcd. for C_3H_6OS: C, 40.03. Found: C, 40.85.

Phosphorus Pentasulfide and Ethyl Orthoformate.—Twenty-two grams of phosphorus pentasulfide (0.1 mole) and 60 g. of ethyl orthothioformate (0.33 mole) were heated with agitation at 110–115° for one hour. The reaction mixture was immediately subjected to vacuum distillation. At a pressure of 0.8 mm. 6 g. of a viscous orange liquid was collected at 40–60°; 29.5 g. (60%) of triethyl tetrathiophosphate at 97–100°; $n^{20}D$ 1.6201; and 31.5 g. (99%) of a mobile orange liquid was collected in the Dry Ice trap. On standing overnight, the liquid collected in the Dry Ice trap became very viscous, and it could not be distilled at 0.5 mm. without decomposition. By analogy with the phosphorus pentoxide–ethyl orthoformate reaction this material may be ethyl dithioformate.[9]

Anal. Triethyl tetrathiophosphate. Calcd. for $C_6H_{15}S_4P$: S, 52.05; P, 12.57. Found: S, 52.08; P, 12.06. Ethyl dithioformate. Calcd. for $C_3H_6S_2$: S, 60.4. Found: S, 59.2.

Phosphorus Pentoxide and Ethyl Orthothioformate.—Fourteen grams of phosphorus pentoxide and 60 g. of ethyl orthothioformate were heated with agitation for 2 hours at 140°. The mixture was subjected to vacuum distillation at 0.4 mm. giving 41.2 g. of ethyl orthothioformate at 55–57° as the only distillable substance.

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[6] B. Holmberg, *Ber.*, **40**, 1740 (1907).

[7] Tetraethyl pyrophosphate was determined by the method of N. M. Dvornikoff and H. L. Morrill, *Anal. Chem.*, **20**, 935 (1948). Triethyl phosphate was determined by a procedure which has been in use in these laboratories. In this procedure, the sample is subjected to alkaline hydrolysis in the presence of benzene for one hour at room temperature, whereby all of the polyphosphate esters are hydrolyzed to acids. Triethyl phosphate, which is not hydrolyzed under these conditions, is then extracted from the alkaline solution with benzene, and the weight and refractive index of the benzene phase determined. By means of a curve of refractive index *vs.* the per cent. triethyl phosphate in water-saturated benzene solutions, the per cent. triethyl phosphate in the sample is calculated. The presence of non-phosphorus compounds can, of course, interfere with this determination.

[8] P. S. Pishchimuka, *J. Russ. Phys.-Chem. Soc.*, **44**, 1406 (1912) [*C. A.*, **7**, 987 (1913)] reports O,O,S-triethyl dithiophosphate, b.p. 128° at 20 mm., and O,S,S-triethyl dithiophosphate, b.p. 148° at 20 mm. Although the boiling point of the former is in agreement with that of the compound obtained from phosphorus pentasulfide and ethyl orthoformate, it is not considered sufficient evidence for definite structural assignment.

[9] T. G. Levi, *Atti reale accad. nazl. Lincei*, [6] **9**, 170 (1929) [*C. A.*, **23**, 3438 (1929)] reports ethyl dithioformate to exist as the trimer, but gives no physical properties.