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Chemistry of Aerofloats and Xanthates. I

Oxidation and Chlorination of O, O-Dialkyl Dithiophosphoric Acids*

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Synopsis

O, O-dialkyl dithiophosphoric acids were prepared by the usual method and were subjected to distillation in vacuo. O, O-diethyl dithiophosphoric acid (b. p. 92–94°C at 9 mm) was treated with chlorine and tetraethyl tetrathio phosphate and chloride were obtained.

In the course of a study of the chemistry of aerofloats and xanthates it became necessary to obtain informations concerning the chlorides of these two series of compounds in order to synthesize their derivatives. Although there has been a rapid growth of literature concerning phosphorus containing organic compounds since the discovery of their insecticidal properties, very little is known regarding essential nature of aerofloats compared with that of xanthates. The main difference of chemical construction of aerofloats and xanthates lies in their central groups, PSSH of the former in lieu of CSSH of the later.

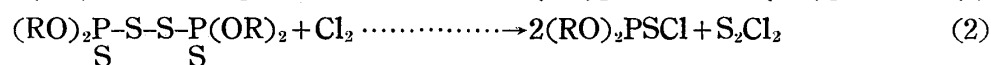
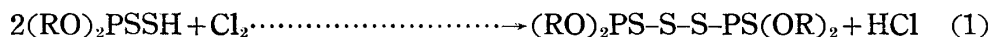
As is well known, free xanthogenic acids bearing alkyl groups of lower carbon numbers are unstable in air and exist only as a form of xanthogenates, while that of aerofloats are, according to the author's results, comparatively stable in dryness. Therefore, chlorides of xanthates are obtained only by treating alkali xanthogenates with certain chlorinating reagents, such as phosphorus pentachloride. Attempts were made to prepare the chlorides of aerofloats by the condensation of phosphorus sulfochloride and alcoholates,^{1–4} the direct chlorination of O, O-dialkyl dithiophosphoric acids with chlorine^{5–6} and the reaction of chlorination reagent and alkali salt of the acids.

According to Fletcher, the chloride was prepared by the chlorination of crude O, O-dialkyl dithiophosphoric acids at the temperature between 25°C and 35°C with about 60 percent of yield. He postulated the reaction mechanisms without isola-

* The 36th report of the Research Institute of Mineral Dressing and Metallurgy.

- (1) J. H. Fletcher, J. C. Hamilton, I. Hechenbleidner, E. I. Hoegberg, B. J. Sertl and J. T. Cassaday, *J. Am. Chem. Soc.* **70** (1948), 3943.
- (2) A. D. F. Toy and T. M. Beck, *Ibid.* **72** (1950), 3191.
- (3) T. W. Mastin et al., *Ibid.* **67** (1945), 1662.
- (4) The reports which were presented by Thurston and Coats were also referenced by Fletcher, Toy and Mastin.
- (5) J. H. Fletcher et al., *Ibid.* **72** (1950), 2461.
- (6) L. Malatesta, *Ital. patent*, 458, 770 (July 28, 1950), *C. A.* **45** (1951), 9555.

ting the intermediate as follows:



The method which Malatesta patented was the same as Fletcher's but the characteristics of his method were that first he used the distillate, b. p. 85–90°C at 4–5 mm, obtained from the product of phosphorus pentasulfide and ethyl alcohol, and second he chlorinated the distillate in the atmosphere of nitrogen.

Before his article on his patent was given in Chemical Abstract, November 1951, the present author had reported in Japanese⁷⁾ that the acids might be capable of being distilled with some decomposition. By repeating the distillation in vacuo, pure products tolerable for analysis were obtained and their purities were ascertained by standard alkali solution. Melting point measurement and analysis of lead and potassium salts led from the distillates also proved that they were the acid derivatives as expected. But the reaction between phosphorus pentasulfide and alcohols is very complicated and many unknown facts were left in future.

Chlorination was performed on O, O-diethyl dithiophosphoric acid in the presence of solvents, such as benzol or carbontetrachloride. When the reaction proceeded in accordance with the postulation presented by Fletcher, it might be expected that the weight of the solution would show no increase in the course of the

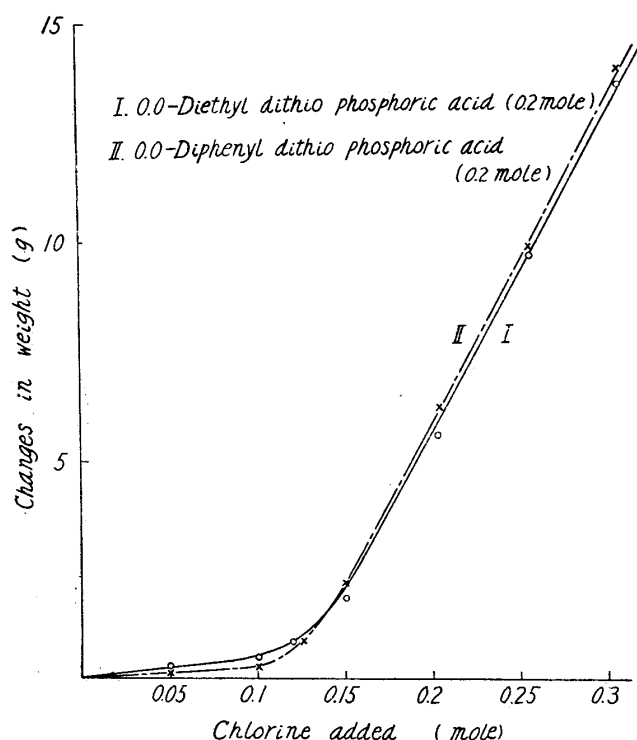


Fig. 1 Relation between the Chlorine Added and Changes in Weight in the Reaction of 0,0-Diethyl Dithiophosphoric Acid (I) or 0,0-Diphenyl Dithiophosphoric Acid (II) and Chlorine.

reaction (1), for the reaction is a dehydrogenating one, while in the course of the reaction (2), the weight would increase proportionally to the amount of chlorine introduced. In experiments designed to investigate this fact, various amounts of chlorine (from 0.05 to 0.3 mole) were introduced to a solution of O, O-diethyl dithiophosphoric acid (0.2 mole) in benzol (60 cc) at 400–500 cc per minute under cooling. Solution was weighed after each amount of chlorine was passed. The results are shown in Figure 1.

From the results, the anticipation that the reaction might proceed in accordance with the postulation above mentioned was in a certain degree confirmed.

Attempts were made to isolate

(7) T. Yamasaki, Bull. Inst. Min. Dress. Metal. 7 (1951), 117.

the chlorination product prepared by treating O,O-diethyl dithiophosphoric acid with various amounts of chlorine. Sulfur and solvent were removed from the products in each run after the method of Fletcher and the residues were cooled to crystallize tetraethyl perthiophosphate which had been prepared. This compound was confirmed by mixing with an authentic sample of m. p. 71–72°C and no depression of m. p. was observed.

The perthio compound was filtered and the filtrates were subjected to distillation in vacuo. The results are shown in Table 1. Chloride was confirmed by its boiling point, refractivity and the melting point of phenylhydrazid led from the chloride, while the acid recovered was also ascertained by its boiling point and the melting point of its lead salt. Other unknown compound was obtained together with compounds isolated but this may be the products prepared by the decomposition of the perthio phosphate or acid and they will also be discussed in future.

Since tetraethyl perthiophosphate was isolated as an oxidation product of O,O-diethyl dithiophosphoric acid with chlorine, it became necessary to ascertain whether the perthio ester could be chlorinated with chlorine. Benzol solutions of perthio ester (0.1 mole) was treated with various amount of chlorine under cooling and the products were treated as before. The results are shown in Table 2.

Table 1. Reaction products of O,O-diethyl dithiophoric acid with chlorine. (Acid: 0.2 mole)

Chlorine Added Mole	Perthio Compd %	Chloride %	Unreacted Acid %	Residue %
0.05	38.2	trace	56.0	—
0.10	62.7	22.0	8.9	—
0.12	51.1	29.5	—	—
0.15	43.5	36.6	—	4.4
0.20	30.9	43.5	—	11.5
0.30	—	70.8	—	19.1

Table 2. Reaction products of O,O-tetraethyl tetrathio diphosphate with chlorine. (Perthiophosphate: 0.1 mole)

Chlorine Added Mole	Unreacted Perthio Compd %	Chloride %	Residue %
0.05	77.7	18.9	—
0.10	54.1	39.7	—
0.15	24.5	50.3	10.2
0.20	—	70.2	25.5

Experimental

Preparation of O,O-dimethyl and diethyl dithiophosphoric acids. In a four-necked flask equipped with a stirrer, a dropping funnel, a thermometer and a reflux condenser with a tube led to a hood, was placed finely ground phosphorus pentasulfide (0.2 mole, m. p. 245–50°C), and appropriate solvents (60–80 cc), such as benzol, xylol, carbontetrachloride and carbondisulfide. Alcohol (0.8 mole) was added through the dropping funnel over a period of about 30 minutes, while the reaction

temperature was maintained at the boiling points of the solvents. In a case of methanol, carbondisulfide was not preferable, for O, O, S-trimethyl thiophosphate was produced with fairly high yield. Stirring was continued for one additional hour to complete the reaction, then the mixture was filtered to remove unreacted phosphorus pentasulfide. The solvent was removed by distillation under reduced pressure and the residue was kept at room temperature to precipitate sulfur, a product of an unexplainable reaction. Sulfur was removed by filtration and the filtrate was subjected to distillation in vacuo. The temperature of oil bath should be kept below 130°C and 140°C for methyl and ethyl respectively, or the reaction mixture was decomposed with violence. The crude filtrate was subjected to re-distillation and the experimental data are given in Table 3.

Table 3. O, O-dialkyl dithiophoric acids. (RO)₂PSSH

R	Solvents	B. p. °C	Mm.	d	Yield %
CH ₃	CCl ₄	81-82	9	1.1785	68
CH ₃	CS ₂				40
CH ₃	C ₆ H ₆				73
C ₂ H ₅	CCl ₄	92-93	9	1.1768	80
C ₂ H ₅	C ₂ S ₅				75
C ₂ H ₅	C ₆ H ₆				73
C ₂ H ₅	C ₆ H ₅ CH ₃				65
C ₂ H ₅	C ₆ H ₄ (CH ₃) ₂				65

The same methods were applied to the product of n-propyl and n-butyl alcohols and phosphorus pentasulfide and the fractions of 113-116°C at 10 mm and 128-132°C at 7.5 mm were obtained respectively. The fraction obtained from ethanol was identified by its lead compound, m. p. 74°C, prepared by adding water-alcohol solution of lead acetate to the alcoholic solution of this fraction and by its oxidation product, m. p. 71-72°C, with sulfuric acid. The melting points of these compounds coincided with the results obtained by Pishchimuka⁸⁾ and Johnson⁹⁾ and mixed m. ps with authentic samples prepared by their methods were undepressed respectively. The m. ps of potassium salts, led from methanol and n-propyl alcohol, 188°C and 166°C respectively, coincided with the results of Hoegberg,¹⁰⁾ while the one from ethanol, contrary to that of Mastin,³⁾ gave a fairly higher melting point of 183°C.

Anal. Calcd. for C₅H₂₀O₄P₂S₄Pb: Pb, 35.85: P, 10.79: S, 22.35.

Found: Pb, 35.85: P, 10.99: S, 22.4

Preparation of metallic salts of the acids. Acetic acid or alcoholic solution of lead acetate, zinc chloride and cadmium acetate were added to the alcoholic solution of appropriate O, O-dialkyl dithiophosphoric acids and the precipitate were collected by filtration subsequent to recrystallization with alcohol or benzol. The other method was that the potassium salts of the appropriate acids dissolved in water were treated with aqueous solution of inorgano-metallic salts to obtain the compounds expected. Lead salts were insoluble in water and slightly soluble in alcohol

(8) P. Pishchimuka, J. pr. Chem., **84** (1911), 748.

(9) B. L. Johnson, U. S. patent 1,763,852, Oct. 31, 1928, C. A.

(10) E. I. Hoegberg and J. T. Cassaday, J. Am. Chem. Soc. **73** (1951), 557.

and petroleum ether and zinc salts of methyl salt was soluble in water while that of the one from ethyl alcohol was hardly soluble in water. Nickel salts were beautiful violet crystals, insoluble in water and soluble in alcohol, benzol and acetone. Cadmium salts were colorless, easily soluble in alcohol and acetone and hardly soluble in benzol and petroleum ether. M. ps. of these salts are shown in Table 4.

Table 4. Melting points of organo-metallic compounds derived from O, O-dialkyl dithiophosphoric acids. °C

	CH ₃	C ₂ H ₅	n-C ₃ H ₇	n-C ₄ H ₉
Hg	136	123	63	61
Zn	decomp. 124	decomp. 189		
Cd	155	149	56-7	48
Pb	119-20	74	43-4	25
Ni	114 ³⁾	105 ³⁾	58	

All the melting points reported in here were uncorrected.

Preparation of O, O-diphenyl dithiophosphoric acid. The acid was prepared from phenol and phosphorus pentasulfide by the method described by Fletcher and it had a melting point of 63°C.

The experiment to investigate the weight of the solution as a function of chlorine introduced. 0.2 mole of O, O-diethyl dithiophosphoric acid (b. p. 92-94°C at 9 mm) and 60 cc of benzol or carbontetrachloride were placed in a four-necked flask provided with a stirrer, a thermometer, a gas inlet tube, the end of which was immersed below the surface of the mixture, and a reflux condenser. The upper end of the condenser was led to a trap surrounded by ice and freezing agent. A definite volume of chlorine (from 0.05 mole to 0.3 mole), dried over phosphorus oxide, was introduced into the mixture at 400 to 500 cc per minute, while the temperature was maintained at 25-35°C by occasional cooling with icewater. Stirring was continued for another 10 minutes to complete the reaction and the solution was weighed, then another amount of chlorine was introduced into the solution.

Oxidation and chlorination of O, O-diethyl dithiophosphoric acid. In a flask described above section was placed 0.2 mole of O, O-diethyl dithiophosphoric acid and 60 cc of benzol. A definite volume of chlorine (0.05 mole to 0.3 mole) was introduced in the same way as mention above. After each mole of chlorine was introduced the mixture was poured into water and allowed to stand for, at least, 5 hours. Sulfur and aqueous layer was removed and organic layer was dried over CaCl₂, followed by a removal of benzol under reduced pressure on water bath. The residue was cooled on ice-freezing agent mixture and the precipitate was subjected to filtration. The crystal was washed with petroleum ether (30 cc) and was purified by recrystallization from ethyl alcohol, m. p. 71-2°C. Mother liquor was concentrated on water bath and the procedure repeated until no more precipitate was given out. The residue was subjected to distillation in vacuo. Fractions of

82-4°C, 84-95°C and 95-98°C at 10 mm respectively were collected. Fraction 1 was neutral and the reaction with phenylhydrazine gave a phenylhydrazid, m. p. 68-9°C, and the fraction 3 was acidic and lead salt was obtained by treating with lead acetate. There were no depressions in their m. ps. when mixed with the authentic samples prepared after the methods Mastin⁶⁾ and Johnson¹¹⁾ respectively. The fraction (84-95°C at 10 mm) was treated with a alcohol-K₂CO₃ mixture and the acidic part was removed. Neutral part was identified by its phenylhydrazide and acid salt by its lead salt, each of which was added respectively to the fraction 1 and 3.

Chlorination of tetraethyl tetrathio phosphate with chlorine 0.1 mole of tetraethyl tetrathio phosphate and 60 cc of benzol was placed in a flask described in the above section and a definite amount of chlorine was introduced. No violent evolution of gas was seen as in the case of the above section. After the reaction was completed the products were treated as mentioned before.

Acknowledgement

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