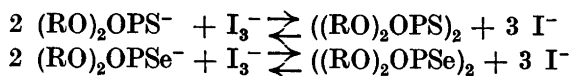


Di-O-alkylmonothiophosphates and Di-O-alkylmonoselenophosphates and the Corresponding Pseudohalogens

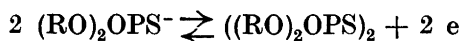
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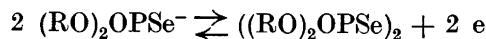
The present paper contains a study on a new type of thio and seleno pseudohalides and pseudohalogens, *viz.*, di-O-alkylmonothiophosphates $(\text{RO})_2\text{OPS}^-$ and di-O-alkylmonoselenophosphates $(\text{RO})_2\text{OPSe}^-$, and their dimeric oxidation products $((\text{RO})_2\text{OPS})_2$ and $((\text{RO})_2\text{OPSe})_2$. Some of the salts have been prepared by earlier workers (see p. 11), but their pseudohalide nature was not yet recognized. It is demonstrated in the present work (pp. 17—22) that measurable equilibria exist between the said salts and iodine:



The redox potentials of the systems



as calculated from equilibrium constants, differ but — 0.02 to + 0.06 volts (in dependence of the nature of the alkyl group R) from that of iodine-iodide. Those of the systems



are 0.19 volts less negative than those of the corresponding thio systems.

The term pseudohalogen was introduced 1925 by Birchenbach and Kellermann¹ as characteristic for some inorganic radicals, the physical and chemical

* The author wishes to express his thanks to Norges Tekniske Høgskoles Fond for a grant.

properties of which resemble those of the real halogens. The principal radicals coming within this category are those of cyanide, cyanate, thiocyanate, selenocyanate, tellurocyanate, azide, and azidodithiocarbonate.

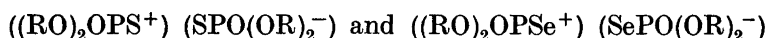
A general account of pseudohalogens is by Walden and Audrieth.²

The term may be extended to include all types of compounds built up by combination in pairs of radicals formed by loss of one electron from a stable, electronegatively charged group.

The reactive bond of halogens and pseudohalogens is a single covalent bond between atoms of the same kind. In reactions, the pseudohalogens, like the halogens, should be capable of undergoing radical fission (electron-pairing) as well as polar fission (electron-sharing).

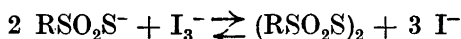
Thus the following types of compounds may be included in the pseudohalogen list:

1. $((\text{RO})_2\text{OPS})_2$ and $((\text{RO})_2\text{OPSe})_2$. Various oxidation reactions, presumably proceeding by a radical mechanism, are demonstrated pp. 22—29. Polar fission, in the sense

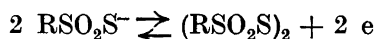


takes place in the hydrolysis reactions, and in the reactions of the thio compounds with *assym. bis-(p-dimethylaminophenyl)-ethylene*.

2. $(\text{RSO}_2\text{S})_2$. It was found^{3,4} that ethanethiosulphonate and *p*-toluene-thiosulphonate give equilibria with iodine:



From the preliminary experiments made (*l. c.*) the redox potentials of the systems



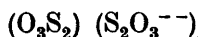
seem to be but 0.03 — 0.05 volts less negative than that of iodide-iodine. Aromatic compounds of the type $(\text{RSO}_2\text{S})_2$ were studied by Otto and Troeger,⁵ Troeger and Hornung,⁶ and Christiansen.⁷ They have a tendency to undergo rearrangement as follows:



In the aliphatic series they have not yet been isolated, though the existence of $(\text{C}_2\text{H}_5\text{SO}_2\text{S})_2$ is indicated through the said equilibrium with iodide-iodine.

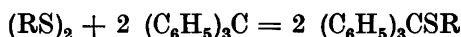
An appropriate nomenclature for the pseudohalogens $((\text{RO})_2\text{OPS})_2$, $((\text{RO})_2\text{OPSe})_2$ and $(\text{RSO}_2\text{S})_2$ may be dialkylthiophosphatogens, dialkylselenophosphatogens, and thiosulphonatogens, respectively.

3. Tetrathionate. As demonstrated in a previous paper,⁴ tetrathionate in reactions with cyanide ion, sulphite ion, sulphinate ions, and small amounts of ethylxanthate ion undergoes polar fission in the sense

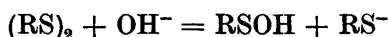


thus showing halogen characteristics. A radical mechanism, to a predominant extent, may be assumed to apply in the oxidation by tetrathionate of mercaptides,⁸ dithiocarbamates,⁹ xanthates,¹⁰ salts of monothio¹¹ and dithio¹⁰ carboxylic acids, and sulphide.¹²

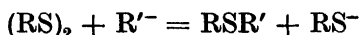
4. Organic disulphides (including carbonic acid derivatives, such as xanthylidisulphides, thiocarbamyldisulphides, and aroyldisulphides) and diselenides. Disulphides are capable of oxidizing sulphide ion,^{13, 14, 15} and react with metals to give mercaptides.^{16, 17, 18} Other radical reactions are those with triphenylmethyl:^{17, 19}



Typical examples of polar fission are the reactions with hydroxyl ion (for literature references see Schöberl²⁰):



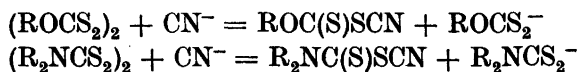
alkali phenate and triphenylmethide:¹⁹



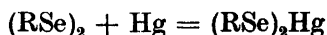
amines:²¹



and cyanide ion (first step):^{4, 11}



Radical fission of diselenides is encountered in reactions with mercury:²²



polar fission in their hydrolysis reactions²³ and in their reactions with alkali-metallorganic compounds.¹⁹

It appears that the thio pseudohalogens may be arranged into three classes with regard to oxidizing properties:

I. Those which give measurable equilibria with iodide, *viz.*, thiocyanogen, dialkylthiophosphatogens, and thiosulphonatogens. The potential of the thiocyanogen-thiocyanate electrode is -0.77 volts.²⁴ The equilibrium of thiocyanate with iodine has been demonstrated by the present author.^{3, 4}

II. Tetrathionate. According to Zimmermann and Latimer²⁵ the potential of the tetrathionate-thiosulphate electrode is -0.10 volts. The value reported by Scheffer and Böhm,²⁶ *viz.*, -0.4 volts, is obviously incorrect, since thiosulphate is able to reduce di-*iso*-propylselenophosphatogen (see p. 28), the potential of which is -0.31 volts.

III. Organic disulphides. They may be obtained from the respective anions (thiocarbonyl anions and mercaptides) by oxidation with tetrathionate (see p. 10). The redox potentials of the systems are low, *e. g.*, that of cysteine-cystine $+ 0.390 \pm 0.043$ volts.^{27, 28a}

A preliminary report on the results of the present investigation has been published.²⁹ The new method employed for the preparation of di-O-alkylmonothiophosphates and selenophosphates (pp. 12—16) was discovered 1942—43.^{4, 30} The equilibrium of di-O-methylmonothiophosphate with iodine was first investigated 1943.^{3, 4}

DI-O-ALKYLMONOTHIOPHOSPHATES AND DI-O-ALKYLMONOSELENOPHOSPHATES

Esters of thiophosphoric acids were first studied by Carius.³¹ He prepared di-O-ethylmonothiophosphoric acid $(C_2H_5O)_2OPSH$ and its salts

(1) by the action of ethanol on phosphorus pentasulphide, and

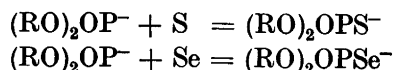
(2) by saponification of the triethyl ester $(C_2H_5O)_3PS$.

Pistschimuka³² prepared various di-O-alkylmonothiophosphates by means of the method (2) of Carius. Emmet and Jones³³ prepared sodium di-O-methylmonothiophosphate and studied its properties in aqueous solutions.

Pistschimuka (*l. c.*) prepared sodium di-O-ethylmonoselenophosphate $(C_2H_5O)_2OPSeNa$ by saponification of the triethyl ester $(C_2H_5O)_3PSe$.

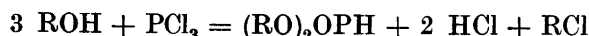
Carius (*l. c.*) said that di-O-ethylmonothiophosphoric acid is a strong acid, its salts being perfectly stable in the solid state. According to Emmet and Jones (*l. c.*) sodium di-O-methylmonothiophosphate is very stable to hydrolysis, its aqueous solutions being neutral to litmus.

A new and convenient method has been worked out for the preparation of di-O-alkylmonothio phosphates and di-O-alkylmonoselenophosphates, *viz.*, by adding sulphur or selenium to the requisite sodium or potassium phosphites in alcohol-ether solutions:



The reactions are rapid and quantitative.

Solutions of alkali dialkylphosphites are readily obtainable from dialkyl hydrogen phosphites $(\text{RO})_2\text{OPH}$ and alcoholic solutions of alkali alkoxide.³⁴ Dialkyl hydrogen phosphites are formed in excellent yields by the action of phosphorus trichloride on alcohol: ^{35, 36, 37, 38}



The alkali dialkyl phosphites are rapidly hydrolysed by water, in anhydrous solvents, however, they are quite stable.

The procedures for preparing sodium and potassium di-O-alkylmonothio phosphates and di-O-alkylmonoselenophosphates are as follows:

0.2 mole sodium or potassium are dissolved in 30—75 ml alcohol (the alcohol corresponding to the dialkyl phosphate to be prepared), and a slight excess (about 0.5 %) of dialkyl hydrogen phosphite, and 60—100 ml ether are added. The ether is essential in effecting a smooth and quantitative process. Sulphur or selenium is added in portions. The reaction takes place vigorously with boiling of the ether, the end being indicated through a rapid change of phenolphthalein to colourless (a crystal added just before the end). Excess of sulphur or selenium is filtered off.

In this way the sodium and potassium methyl, ethyl, *n*-propyl and *iso*-propyl salts have been prepared, and also the potassium *n*-butyl, *iso*-butyl, *sec*-butyl, *iso*-amyl, and *sec*-butylcarbinyl salts. The salts are colourless. From most solvents they separate as needles, which in the case of the sodium salts are very long and thin and distinctly flexible. From petroleum smaller crystals were obtained (sodium propyl and potassium *sec*-butyl salts). Most of them are hygroscopic. The thio salts are perfectly stable in the solid state and in solutions. The seleno salts, if exposed to moist atmosphere and particularly to bright day-light, will assume a red colour on the surface. From aqueous solutions (0.01 *M*) of the seleno salts selenium is sometimes deposited after two or three months.

The salts are readily soluble in water (Pistschimuka ³² said that they were insoluble).

The solubilities of the salts in organic solvents increase with increasing number of carbon atoms in the alkyl groups, however, the *iso*-propyl and *sec*-butyl salts are considerably more soluble than the *n*-propyl and the primary butyl salts, respectively. The sodium salts are more soluble than the corresponding potassium salts, and the seleno salts more soluble than the corresponding thio salts (except for the methyl salts).

These differences in solubility may, partly at least, be explained through a smaller or greater partial covalent character (resonance between purely ionic and purely covalent forms) of the (Na, K) — (S, Se) bonds, increasing covalent character being connected with a higher solubility in non-polar solvents. The percentages of ionic and covalent character are in each case determined by the difference in electronegativity ($K < Na < Se < S$) of the atoms regarded, a small difference corresponding to a high degree of covalence.^{39a} As shown pp. 17—22, the secondary propyl and butyl groups effect a smaller electronegativity of the thio and seleno atoms than do the corresponding primary groups.

The anions probably are resonance hybrids of several electronic structures, as is the phosphate ion.^{39b}

In the case of the amyl compounds the free acids are insoluble in water and separate as oil drops if mineral acids are added. They are apparently quite stable.

For the analysis of the salts, accurate and convenient iodometric methods have been worked out. The thiophosphates are oxidized by iodine in presence of sodium hydroxide:



excess iodine being back-titrated with thiosulphate after addition of sulphuric acid.

The following procedures were adopted:

(1) *0.1 N iodine*. To 25 ml 0.01 *M* di-O-alkylmonothiophosphate (in the case of the amyl compounds 20 ml) are added 10 ml 1 *N* sodium hydroxide and then 25 ml 0.1 *N* iodine. After standing for 5 minutes, 10 ml 4 *N* sulphuric acid are added, and the excess of iodine is back-titrated with 0.1 *N* thiosulphate.

(2) *0.01 N iodine*. To 25 ml 0.001 *M* di-O-alkylmonothiophosphate are added 10 ml 0.1 *N* sodium hydroxide and then 25 ml 0.01 *N* iodine. After standing for 5 minutes, 10 ml 2 *N* sulphuric acid are added, and the solution titrated with 0.01 *N* thiosulphate.

The selenophosphates are oxidized by iodine in sodium hydrogen carbonate buffer:



The selenium is oxidized to selenite. For back-titration of the iodine, acetic acid is added, selenite being indifferent to iodide in acetate buffers.

The following procedures have proved their values:

(1) *0.1 N iodine*. Methyl, ethyl and propyl compounds: To 25 ml 0.01 *M* di-O-alkylmonoselenophosphate are added 2 g sodium hydrogen carbonate and then 20 ml 0.1 *N* iodine. After standing for 5 minutes (stoppered flask), 20 ml 10 per cent acetic acid are added, and the excess of iodine is back-titrated with 0.1 *N* thiosulphate.

In the case of the butyl and amyl compounds a greater excess of iodine must be employed (25 ml 0.1 *N* iodine are added), and the time of standing should be 10 minutes. Moreover, in the case of the amyl compounds 10 ml 96 % ethanol were added prior to iodine, in order to increase the rate of resolution of insoluble intermediates.

(2) *0.01 N iodine*. To 25 ml 0.001 *M* di-O-alkylmonoselenophosphate are added 2 g sodium hydrogen carbonate and 25 ml 0.01 *N* iodine. After standing for 15 minutes, 20 ml 10 per cent acetic acid are added, and the excess of iodine is back-titrated with 0.01 *N* thiosulphate.

The methods give accurate and self-consistent results.

Experimental

The dialkyl hydrogen phosphites were prepared from phosphorus trichloride and the anhydrous alcohols by the method used by Nylén in the case of the ethyl compound.³⁸ Three new compounds were included: *sec*-Butyl $(\text{C}_4\text{H}_9\text{O})_2\text{OPH}$, b. p.₁₂ 101°C, *iso*-amyl $(\text{C}_5\text{H}_{11}\text{O})_2\text{OPH}$, b. p.₁₀ 133°C, *sec*-butylcarbonyl $(\text{C}_5\text{H}_{11}\text{O})_2\text{OPH}$, b. p.₁₅ 142°C. Yields 40—50 % methyl compound, 80—90 % ethyl and higher primary alkyl compounds, and 60—70 % *iso*-propyl and *sec*-butyl compounds.

The methyl and ethyl alcohol used in preparing the di-O-alkylmonothiophosphates and selenophosphates had been dried by distilling over magnesium, and in the case of the other alcohols carefully rectified products were employed. In order to avoid rearrangement the same alcohol should be employed as that corresponding to the dialkyl phosphate which is to be prepared.

The sulphur (flowers or rhombic) or selenium (preferably red) were added in portions so as to keep the ether gently boiling during the reaction.

The selenium reacted somewhat smoother than did sulphur, and it is advisable to warm the solution gently before the first portion of selenium is added. When reaction has ceased the excess sulphur or selenium is filtered off (crystals of thiophosphate or

selenophosphate which have separated out may be dissolved by heating). In most cases the products were isolated by evaporation of the alcohol-ether (partly or completely) *in vacuo*. This was effectively and rapidly achieved through attaching the flask directly to the vacuum pipe, omitting the capillary and the condenser, and swirling the flask gently in a water or calcium chloride bath so as to prevent splashing.

The various solvents employed for isolation and recrystallization had all been carefully dried. The petroleum boiled at 80—100° C. Chloroform Ph. N. (containing ethanol) was employed in the case of the ethyl compounds. For all other purposes the ethanol was removed by means of concentrated sulphuric acid, and the chloroform stabilized by addition of two parts per thousand of petroleum.⁴⁰

The general procedure (see p. 12) was employed. The amounts of alcohol and ether reported beneath refer to 0.2 mole sodium (4.6 g) or potassium (7.8 g), and 0.201 mole dialkyl hydrogen phosphite.

Sodium di-O-methylmonothiophosphate and di-O-methylmonoselenophosphate. 50—60 ml methanol, 60 ml ether. The products will crystallize on cooling, and may be more completely isolated through partial evaporation and addition of ether. Recrystallization: 5 g from 50 ml methylacetate and 3 ml methanol. 50 ml ether may be added. Or 5 g from 120—150 ml pure methylacetate. Insoluble in ether and chloroform, readily soluble in pyridine.

Sodium di-O-ethylmonothiophosphate and di-O-ethylmonoselenophosphate. 60 ml ethanol, 60 ml ether. Isolated as above. Recrystallization: 5 g thio salt are dissolved in 50 ml chloroform (Ph. N.), 5 g seleno salt in 30 ml chloroform (Ph. N.). 50 ml ether are added. Practically insoluble in ether, slightly soluble in pure chloroform (0.01 *M* solutions of the thio salt may be prepared).

Sodium di-O-n-propylmonothiophosphate and di-O-n-propylmonoselenophosphate. 60—80 ml *n*-propanol, 60 ml ether. Evaporated to dryness, dissolved in benzene, and petroleum added. Recrystallization: 5 g thio salt from 10 ml benzene (20 ml petroleum are added) or from 80 ml petroleum. 5 g seleno salt from 25 ml petroleum (soluble in 10 ml hot petroleum). Readily soluble in ether.

Sodium di-O-iso-propylmonothiophosphate and di-O-iso-propylmonoselenophosphate. 60—80 ml *iso*-propanol, 60 ml ether. Evaporated to dryness, dissolved in petroleum, and cooled. Recrystallized from petroleum (5 g from 25 ml). Readily soluble in ether and benzene.

Potassium di-O-methylmonothiophosphate and di-O-methylmonoselenophosphate. 30 ml methanol, 80 ml ether. The seleno salt crystallized on cooling, and 100 ml ether were added. The thio salt was evaporated nearly to dryness, and ether added. Recrystallization (thio and seleno): 5 g are dissolved in 15 ml pyridine, and 30 ml ether are added. Readily soluble in acetone, sparingly soluble in methylacetate.

Potassium di-O-ethylmonothiophosphate and di-O-ethylmonoselenophosphate. 50 ml ethanol, 80 ml ether. The salts crystallize excellently. Isolated by cooling and addition of 100 ml ether. Recrystallized from ethylacetate (5 g thio salt dissolved in 50 ml, 5 g seleno salt in 20 ml. 50 ml ether are added). Practically insoluble in ether.

Potassium di-O-n-propylmonothiophosphate and di-O-n-propylmonoselenophosphate. 60 ml *n*-propanol, 100 ml ether. Only the thio salt crystallized on cooling. The seleno salt was isolated through evaporation nearly to dryness, and addition of ether. Recrystallization: 5 g thio salt from 50 ml chloroform and 2 ml *n*-propanol. 50 ml ether are added. Or from 15 ml *n*-propanol (30 ml ether added). 5 g seleno salt from 50 ml chloroform (50 ml ether added).

Potassium di-O-iso-propylmonothiophosphate and di-O-iso-propylmonoselenophosphate. 60 ml *iso*-propanol, 100 ml ether. Evaporated to dryness, dissolved in chloroform, and ether added. Recrystallized from chloroform (5 g thio salt in 20—25 ml, 50 ml ether are added). The seleno salt is more soluble).

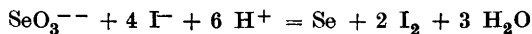
Potassium di-O-n-butylmonothiophosphate, di-O-n-butylmonoselenophosphate, di-O-iso-butylmonothiophosphate, and di-O-iso-butylmonoselenophosphate. 60 ml *n*-butanol and *iso*-butanol, respectively, 100 ml ether. The thio salts crystallized on cooling and were further precipitated by addition of 200 ml ether. Recrystallized from chloroform (5 g dissolved in 50 ml, 50 ml ether added). Seleno salts: Evaporated to dryness, dissolved in benzene, and petroleum added. Recrystallized from benzene-petroleum or from chloroform-ether (5 g dissolved in 15 ml chloroform, 30 ml ether added). Sparingly soluble in ether.

Potassium di-O-sec-butylmonothiophosphate and di-O-sec-butylmonoselenophosphate. 60 ml *sec*-butanol, 100 ml ether. Evaporated to dryness, dissolved in petroleum, and cooled. Recrystallized from petroleum (5 g thio salt from 50 ml, 5 g seleno salt from 25 ml). Readily soluble in ether, benzene, carbon tetrachloride.

Potassium di-O-iso-amylmonothiophosphate, di-O-iso-amylmonoselenophosphate, di-O-sec-butylcarbinylmonothiophosphate, and di-O-sec-butylcarbinylmonoselenophosphate. 75 ml *iso*-butylcarbinol and *sec*-butylcarbinol, respectively, 100 ml ether. The thio salts crystallized on cooling. 200 ml ether were further added. Seleno salts: Evaporated to dryness, dissolved in chloroform, and ether added. Recrystallized from chloroform (5 g thio salt dissolved in 30 ml, 5 g seleno salt in 15 ml, 50 ml ether added).

In order to save space the figures for the iodometric analyses of the salts are not included. All the salts were analyzed by the said methods, the found percentages of sulphur and selenium ordinarily differing but 0.1—0.2 relative per cent from the theoretical values. The titration values for equal samples of separate salts usually agreed within less than 0.02 ml.

In the case of the seleno salts 2 g potassium iodide and 20 ml 4 *N* sulphuric acid may be added to the titrated solutions, the following reaction taking place:



A second titration with thiosulphate may thus be carried out. The results, however, are sometimes too low,⁴¹ and the end point is difficult to observe because of the liberation of finely divided selenium.

Phosphorus analyses were made volumetrically by means of the method of Neumann (for references see Nylén³⁸). Selenium was determined gravimetrically according to Fredga,²² by heating the substance with concentrated sulphuric acid and nitric acid,

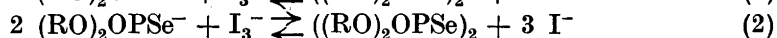
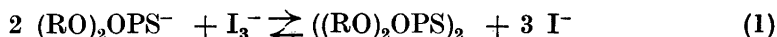
and precipitating the selenium by means of hydrazine sulphate. For phosphorus analysis in the filtrate it was diluted to 500 ml, and 100 ml pipetted out, 5 ml concentrated nitric acid added, and excess hydrazine destroyed by means of potassium nitrite. After boiling for some time the phosphate was determined according to Neumann.

0.08388 g (C₂H₅O)₂OPSK: 23.19 ml 0.4845 N NaOH.
Calc. P 14.9. Found P 14.8.

0.4829 g (C₂H₅O)₂OPSeK: 0.1496 g Se, 5 · 21.82 ml 0.4845 N NaOH.
Calc. Se 30.9, P 12.1. Found Se 31.0, P 12.1.

THE EQUILIBRIA OF DI-O-ALKYLMONOTHIOPHOSPHATES AND DI-O-ALKYLMONOSELENOPHOSPHATES WITH IODINE. INDUCTIVE EFFECTS OF ALKYL GROUPS

This section contains a study on the reversible equilibria:



The equilibria are established in neutral and in acid aqueous solutions. The di-O-alkylmonoselenophosphates are more readily oxidized by iodine than are the corresponding thio salts, the latter being indifferent to iodine in presence of iodide. In absence of iodide the di-O-alkylmonoselenophosphates are almost quantitatively oxidized by iodine, in presence of iodide only partly.

The alkyl groups R were found to exert a marked influence on the position of the above equilibria. In the case of (1) it is progressively displaced to the right in the order R = methyl, ethyl, *n*-propyl, primary butyl, *iso*-propyl, *sec*-butyl, and primary amyl. The same sequence was found to hold for the methyl, ethyl, *n*-propyl, and *iso*-propyl seleno compounds.

Within the primary alkyl groups the magnitude of the effect thus depends on the total number of carbon atoms, branching of the chains (butyl and amyl) having no observable influence. Secondary alkyl groups exert a stronger influence than do the primary groups.

The observed effect of the alkyl groups is due to their electron-repelling (electron-release) effect, in terms of the electronic theory of the English school ^{28b} the + *I*_s effect. This is a static effect characteristic of a molecule in equilibrium with its environments. Except for the non-influence of branching of the primary butyl and amyl groups the sequence observed is in accordance with the order usually assigned to the + *I*_s effect of alkyl groups: ⁴² Methyl < Ethyl < *n*-Propyl < *n*-Butyl < *iso*-Propyl.

The case provides an example of $+I_S$ effect of alkyl groups investigated by a purely static method.

The stoichiometric validity of Eq. (1) has been confirmed at three different concentrations of di-O-alkylmonothiophosphate for R = methyl, ethyl, n -propyl, and *iso*-propyl, and hence it may be assumed to apply also for the butyl and amyl compounds. For the equilibrium constants at room temperature of the equilibria (1)

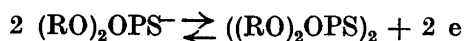
$$K^S = \frac{[(RO)_2OPS] [I^-]^3}{[(RO)_2OPS^-]^2 [I_3^-]}$$

see table 1.

Table 1. Di-O-alkylmonothiophosphate systems.

R	K^S	E_O^S	ΔE_R^S
Methyl	0.2	— 0.56	0
Ethyl	1.5	— 0.53	0.03
n -Propyl	3.6	— 0.52	0.04
n -Butyl	7	— 0.51	0.05
<i>iso</i> -Butyl			
<i>iso</i> -Propyl	24	— 0.50	0.06
<i>sec</i> -Butyl	56	— 0.49	0.07
<i>iso</i> -Amyl	110	— 0.48	0.08
<i>sec</i> -Butylcarbiny			

The redox potentials E_O^S of the systems



were calculated from the equilibrium constants K^S by means of the equation:

$$E_O^S = E_O^I - \frac{RT}{2F} \ln K' / K^S$$

Here E_O^I is the standard potential of the iodine-iodide electrode (at unit activity), viz., —0.62 volts, and K' is the dissociation constant of the triiodide ion, viz., 0.0014 at 25° C.⁴³ Omitting corrections for temperature, we have:

$$E_O^S = -0.54 + 0.029 \log K^S$$

The values so obtained are listed in the third column of table 1.

The figures of the fourth column are the relative potentials

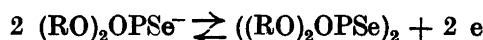
$$\Delta E_R^S = E_{O(R)}^S - E_{O(CH_3)}^S$$

They give a measure for the effect of substitution in the methyl groups of di-O-methylmonothiophosphate.

Measurements of the di-O-alkylmonoselenophosphate equilibria (2) at two different concentrations of iodide gave approximately constant values for the equilibrium constants

$$K^{Se} = \frac{[(\text{RO})_2\text{OPSe}] [\text{I}^-]^3}{[(\text{RO})_2\text{OPSe}^-]^2 [\text{I}_3^-]}$$

The redox potentials E_O^{Se} of the systems



calculated as in the case of the thio systems, are listed in the third column of table 2.

Table 2. *Di-O-alkylmonoselenophosphate systems.*

R	K^{Se}	E_O^{Se}	ΔE_R^{Se}	ΔE_O^{S-Se}
Methyl	$9 \cdot 10^5$	- 0.37	0	0.19
Ethyl	$9 \cdot 10^6$	- 0.34	0.03	0.19
<i>n</i> -Propyl	$2 \cdot 10^7$	- 0.33	0.04	0.19
<i>iso</i> -Propyl	$1 \cdot 10^8$	- 0.31	0.06	0.19

It is interesting to note that the figures for ΔE_K^{Se} ($= E_{O(R)}^{Se} - E_{O(CH_3)}^{Se}$) are identical with those for ΔE_R^S .

Thus the difference between the potentials of the seleno systems and the corresponding thio systems is the same for all the alkyl groups, *viz.*, 0.19 volts.

From the stoichiometric form of Eqq. (1) and (2) it may be concluded that in the case of di-O-alkylmonothiophosphates and di-O-alkylmonoselenophosphates there is no tendency of formation of poly-ions of the type $((\text{RO})_2\text{OPS})_3^-$ and $((\text{RO})_2\text{OPSe})_3^-$.

Experimental

The sodium di-O-methyl, ethyl, *n*-propyl and *iso*-propylmonothiophosphates and selenophosphates were employed, and the potassium salts of the higher alkyl compounds.

Di-O-alkylmonothiophosphates. In examining the equilibrium (1) the following procedure was employed:

To 10 ml aqueous di-O-alkylmonothiophosphate were added 5 ml starch solution (2 parts per thousand), one drop of 10 per cent acetic acid, to prevent hydrolysis, and various amounts of potassium iodide. The volume was adjusted to 25 ml, and the solu-

tion was tested with 0.01 *N* iodine (containing 2 % potassium iodide). The amount of iodide was recorded which had to be present in order that one drop of iodine should produce a stable starch-iodine colour, equal in intensity to that produced by one drop of iodine in 50 ml water containing a few crystals of potassium iodide. The equilibrium constants K^S were calculated from the iodide values so obtained, with the assumption that at this particular intensity the concentration of formed $((RO)_2OPS)_2$ is equal to that of uncombined I_3^- .

The iodine was added from an ordinary buret, the drops having an average volume of 0.03 ml.

Table 3, which gives the amounts of iodine consumed at the said conditions by 10 ml 0.01 *M* thiophosphate, is included in order to illustrate the sensitivity of the method.

Table 3. Amounts of 0.01 *N* iodine necessary for equilibrium.

R	P o t a s s i u m i o d i d e , g								
	0	0.02	0.06	0.10	0.14	0.20	0.30	0.40	0.50
Methyl		4 drops	1 drop						
Ethyl	1.05 ml	0.45 ml	3 drops	1 drop ^b					
<i>n</i> -Propyl	1.10 ml		6 drops	3 drops	1 drop ^b				
<i>n</i> -Butyl	2.7—9 ml ^a		0.7—8 ml ^a	4 drops	2 drops	1 drop			
<i>iso</i> -Butyl	2.6—8 ml ^a		0.5—6 ml ^a	4 drops	2 drops	1 drop			
<i>iso</i> -Propyl	2.1 ml			0.5 ml		5 drops	1 drop		
<i>sec</i> -Butyl	5.9 ml ^a			0.6 ml ^a		0.4 ml ^a	3 drops	1 drop	
<i>iso</i> -Amyl	6.5—9 ml ^a					3.0—2 ml ^a	9 drops ^a		1 drop
<i>sec</i> -Butyl-									
carbonyl	6.5—9 ml ^a					3.0—2 ml ^a	9 drops ^a		1 drop

^aTurbidity ^bVery faint starch-iodine colour

With the methyl, ethyl, *n*-propyl, and *iso*-propyl compounds the solutions remained perfectly clear during the experiments, no insoluble products being formed. In the case of the butyl and amyl compounds, however, the oxidation products $((RO)_2OPS)_2$ are sparingly soluble in water and separated out as a turbidity (butyl compounds after five or six drops of iodine, amyl compounds after four drops). The systems thus became heterogeneous, and more iodine was consumed than would correspond to the true homogeneous equilibria. This is shown by the increase in iodine values when turbidity occurred, and by the fact that if 10 ml 96 % ethanol were added to the turbid reaction mixtures, so as to increase the solubility of the products, iodine was regenerated.

The critical iodide values are given in table 4.

Table 4. *Di-O-alkylmonothiophosphate systems. g KI ($\pm 10\%$) necessary for equilibrium at one drop of iodine.*

R	Molarity of 10 ml di-O-alkylmonothiophosphate			
	0.00354 ($= 0.01 \cdot 2^{-3/2}$)	0.01	0.0283 ($= 0.01 \cdot 2^{3/2}$)	0.08 ($= 0.01 \cdot 4^{3/2}$)
Methyl		0.06	0.12	0.20
Ethyl		0.12	0.22	0.40
<i>n</i> -Propyl		0.16	0.30	0.60
<i>n</i> -Butyl		0.20		
<i>iso</i> -Butyl		0.20		
<i>iso</i> -Propyl	0.15	0.30	0.60	
<i>sec</i> -Butyl		0.40		
<i>iso</i> -Amyl		0.50		
<i>sec</i> -Butylcarbinyl		0.50		

It will be seen that for different concentrations of a single salt the ratio $[I^-]^3 / [(RO)_2OPS^-]^2$ is nearly constant. There seems to be a slight tendency of higher values at lower concentrations of iodide, perhaps (aside from possible variations in activity coefficients) due to displacement to the right of the equilibrium:



which has the equilibrium constant 0.0014 at 25° C.⁴³ Thus 0.06 g and 0.20 g potassium iodide in a volume of 25 ml give $[I_2] / [I_3^-] = 10\%$ and 3%, respectively. The degree of dissociation is small, and no correction for it has been made in calculating the K^S and K^{Se} values.

The chief source of error in the K^S values is the uncertainty in establishing the exact value of the ratio $[(RO)_2OPS^-] / [I_3^-]$ at the chosen equilibrium conditions. It may differ $\pm 50\%$ from unity, which, together with other probable errors, will give a maximal possible error of $\pm 60\%$ in the equilibrium constants, and corresponding errors in the potentials. The relative potentials are more accurate, since the said chief error should remain constant from one measurement to another.

Di-O-alkylmonoselenophosphates. Only the methyl, ethyl, *n*-propyl, and *iso*-propyl systems were examined, these being the only ones that remained homogeneous throughout.

To 10 ml ca 0.01 *M* di-O-alkylmonoselenophosphate (exact concentration determined by iodometric analysis), 5 ml starch solution, and 1 ml 10% acetic acid, were added 1 g or 2 g potassium iodide, and the solution titrated with 0.01 *N* iodine.

Table 5. *Di-O-alkylmonoselenophosphate systems. ml iodine consumed, and calculated equilibrium constants.*

R	Molarity of 10 ml	1 g KI		2 g KI	
		ml	K	ml	K
Methyl	$9.6 \cdot 10^{-3}$	3.0—3.2	$7 \cdot 10^5$	1.0	$10 \cdot 10^5$
Ethyl	$10.2 \cdot 10^{-3}$	7.0	$7 \cdot 10^6$	4.5—5.0	$10 \cdot 10^6$
<i>n</i> -Propyl	$9.9 \cdot 10^{-3}$	7.7—7.9	$1.8 \cdot 10^7$	5.6—5.8	$2.1 \cdot 10^7$
<i>iso</i> -Propyl	$9.8 \cdot 10^{-3}$	8.8—9.0	$1.1 \cdot 10^8$	7.8	$1.4 \cdot 10^8$

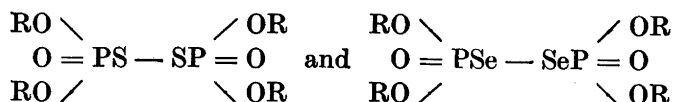
In calculating the equilibrium constants the amount of I_3^- present at equilibrium was taken as half a drop of iodine, viz., $\frac{0.03}{2 \cdot 2} \cdot 10^{-5}$ mole.

The maximal possible error in the equilibrium constants and potentials given for the seleno systems should be of the same order of magnitude as those for the thio systems.

The *iso*-propyl seleno salt being the most readily oxidable, its solutions may be accurately titrated with iodine provided that no extra iodide is added. The solution (0.01 *M*) should be about 1 *N* with respect to sulphuric acid. No sharp end points could be obtained in analogous experiments with the butyl and amyl salts.

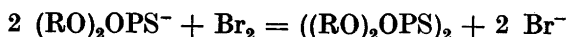
DIALKYLTHIOPHOSPHATOGENS AND DIALKYLSELENOPHOSPHATOGENS

In this section the preparation and properties of the dimeric oxidation products $((RO)_2OPS)_2$ and $((RO)_2OPSe)_2$ are described. The terms dialkylthiophosphatogens and dialkylselenophosphatogens, respectively, will be employed (see p. 10). Their structures presumably are:

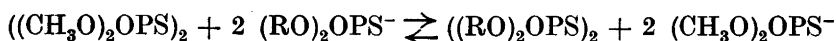


In each series the methyl, ethyl, *iso*-propyl, *iso*-butyl, and *iso*-amyl compounds have been prepared, by the following methods:

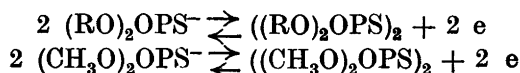
Dialkylthiophosphatogens. The methyl compound by the action of bromine on sodium di-O-methylmonothiophosphate in ether suspension, the ethyl compound by the same method from potassium di-O-ethylmonothiophosphate suspended in petrol ether:



The *iso*-propyl, *iso*-butyl, and *iso*-amyl compounds were prepared from the methyl compound, dissolved in water, and aqueous solutions of the respective potassium di-O-alkylmonothiophosphates:



The equilibrium constants *K* of these equilibria are related to the differences ΔE_R^S (see p. 18) in redox potentials of the systems



by the equation:

$$\Delta E_R^S = \frac{RT}{2F} \ln K$$

Furthermore:

$$K = \left(\frac{\alpha}{1 - \alpha} \right)^3$$

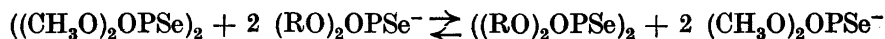
in which α is the degree of displacement from left to right. For methyl/*iso*-propyl $\Delta E_R^S = 0.06$ and thus $\alpha = 83\%$, for methyl/*iso*-butyl $\Delta E_R^S = 0.05$ and $\alpha = 79\%$, for methyl/*iso*-amyl $\Delta E_R^S = 0.08$ and $\alpha = 89\%$. In all three cases the product $((\text{RO})_2\text{OPS})_2$ is insoluble in water and separates as an oil, which causes further displacement of the equilibrium.

The *iso*-butyl compound was also obtained by the action of iodine, dissolved in ether, on an excess of aqueous potassium di-O-*iso*-butylmonothio-phosphate.

The methyl compound $((\text{CH}_3\text{O})_2\text{OPS})_2$ forms colourless crystals which melt at $30.5\text{--}31^\circ\text{C}$. It is hygroscopic, and readily soluble in water and in most organic solvents, slightly soluble in petrol ether. The higher alkyl compounds were obtained as colourless oils, being less soluble in water and more soluble in petrol ether the higher the number of carbon atoms in the alkyl groups. The *iso*-butyl and *iso*-amyl compounds are practically insoluble in water.

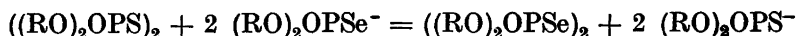
The compounds are quite stable when kept in a dry atmosphere. The oxidizing power of an $0.01\text{ }N$ aqueous solution of the methyl compound is reduced to about half its original value after one hour at room temperature, and after two or three hours sulphur is deposited. Their solutions in inert organic solvents are quite stable.

Dialkylselenophosphatogens. The methyl and ethyl compounds were obtained by the action of iodine, dissolved in ether, on aqueous sodium or potassium di-O-alkylmonoselenophosphate. The *iso*-butyl and *iso*-amyl compounds were prepared from the methyl compound, dissolved in water, and aqueous solutions of the respective di-O-alkylmonoselenophosphates:

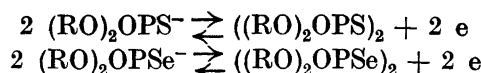


As in the case of the thio compounds the equilibria are further displaced to the right through the insolubility in water of the products.

The dialkylselenophosphatogens may also be obtained from the corresponding thio compounds:



A difference of 0.19 volt (see p. 19) in the redox potentials of the systems

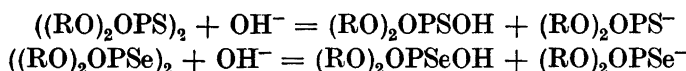


would give $\alpha = 99\%$ for the above change. The ethyl and *iso*-propyl compounds were prepared by this method.

The methyl compound $((\text{CH}_3\text{O})_2\text{OPSe})_2$ forms pale greenish crystals with melting point $3-4^\circ\text{C}$, the higher alkyl compounds are oils. Their solubilities in water and in organic solvents are of the same order of magnitude as those of the corresponding thio compounds. The oils (melts) are green with a brownish tinge, and so are their concentrated solutions (in water and in organic solvents). Dilute solutions have a green colour. In absence of moisture the pure compounds will liberate selenium and thus become red after one or two days. Their solutions in inert organic media are more stable. An 0.01 *N* aqueous solution of the methyl compound liberated selenium after about 10 minutes.

The dialkylthiophosphatogens and dialkylselenophosphatogens are capable of oxidizing iodide (in the case of the seleno compounds only relatively concentrated iodide solutions), thiosulphate (to tetrathionate), and thiocarbonyl salts (to the corresponding disulphides).

With aqueous alkali the thio compounds give a yellow colour, the seleno compounds a brown colour. The hydrolysis probably takes place according to the schemes



in analogy with the hydrolysis reactions of halogens and organic disulphides.

With *assym. bis*-(*p*-dimethylaminophenyl)-ethylene in acetonitril the thio compounds (methyl and ethyl) give a blue colour, as do iodine and bromine.⁴⁴ According to the general scheme⁴⁴ the compounds thereby add to the ethylene linkage, with polar fission in the sense $((\text{RO})_2\text{OPS}^+) (\text{SPO}(\text{OR})_2^-)$.

With aqueous *p*-toluenesulphinat the methyl thio compound immediately gave a semi-solid precipitate, which further solidified on boiling and was dissolved in hot glacial acetic acid. On cooling, crystals of monosulphur di-(*p*-toluenethiosulphonate) $\text{S}(\text{S}_2\text{O}_2\text{C}_6\text{H}_4\text{CH}_3\text{-}p)_2$ separated out. The first step probably is analogous to the reactions of halogens with sulphinates:



The intermediate $\text{RSO}_2\text{SPO}(\text{OCH}_3)_2$ may be unstable and break up to give thiosulphonatogen $(\text{RSO}_2\text{S})_2$, followed by rearrangement ⁵ into $\text{S}(\text{SO}_2\text{R})_2$ and $\text{S}(\text{S}_2\text{O}_4\text{R})_2$ (see p. 9).

The methyl seleno compound does apparently not react with aqueous *p*-toluenesulphinate, however, selenium is rapidly liberated. The catalysis may be due to an equilibrium



the compound $\text{RSO}_2\text{SePO}(\text{OCH}_3)_2$ being the unstable intermediate.

Experimental

Ether solutions of dialkylthiophosphatogens and dialkylselenophosphatogens, which in the course of preparation had been in contact with water, were dried over anhydrous sodium sulphate, and the ether subsequently evaporated off *in vacuo*. Before analysis, the products were dried *in vacuo* over sulphuric acid.

Dialkylthiophosphatogens

(1) To 8 g $(\text{CH}_3\text{O})_2\text{OPSNa}$ suspended in 50 ml abs. ether was added 1 ml bromine. A smooth reaction took place. The solid particles were treated with a glass rod for a few minutes until the bromine colour had vanished, the suspension was then filtered, and the ether evaporated off *in vacuo*. On cooling the remaining oil in a carbon dioxide-acetone freezing mixture it slowly solidified throughout. Crystallization from concentrated ethereal solutions was later effected by cooling and seeding. Colourless crystals, m. p. 30.5—31°C. 0.05061 g subst.: 20.72 ml 0.4845 *N* NaOH (Neumann).

0.08904 g subst.: 0.1469 g BaSO_4 (Grote-Krekeler. Phosphate removed as magnesium ammonium phosphate).

$((\text{CH}_3\text{O})_2\text{OPS})_2$ (282,2) Calc. P 22,0 S 22,7
Found » 21,9 » 22,7

In moist air the crystals liquify, and sulphur is liberated. Stability of aqueous solutions: 20 ml 0.009061 *N* thiosulphate to which had been added 10 ml 4 per cent potassium iodide solution and 5 ml starch solution were titrated with

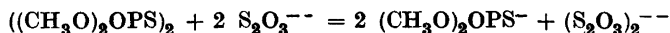
(a) 0.004421 *M* $((\text{CH}_3\text{O})_2\text{OPS})_2$ (0.3118 g per 250 ml) in water

(b) 0.004494 *M* $((\text{CH}_3\text{O})_2\text{OPS})_2$ (0.3170 g per 250 ml) in 1 *N* aqueous sulphuric acid.

Table 6. Stability of aqueous dimethylthiophosphatogen.

Age of solutions in minutes	ml consumed	
	(a)	(b)
3	21.98	21.65
10	23.03	22.52
20	23.91	23.90
30	25.02	25.31
60	29.53	29.49

Sulphuric acid thus has no influence on the stability. The thiosulphate is evidently oxidized to tetrathionate:



(2) The suspension of 9 g $(\text{C}_2\text{H}_5\text{O})_2\text{OPSK}$ in 50 ml petrol ether was cooled in an ice-sodium chloride freezing mixture, and 1 ml bromine in 50 ml petrol ether was added. The mixture was treated as described in the case of the methyl compound. The residual colourless oil did not crystallize even on cooling to -70°C . It did not distill even at 100°C at 0.07 mm Hg (at 150° rapid decomposition took place).

0.05593 g subst.: 19.08 ml 0.4845 *N* NaOH. 0.08654 g subst.: 0.1193 g BaSO_4 .

$((\text{C}_2\text{H}_5\text{O})_2\text{OPS})_2$ (338.3) Calc. P 18.3 S 19.0
Found » 18.3 » 18.9

(3) 3 g $(\text{iso-C}_4\text{H}_9\text{O})_2\text{OPSK}$ (50 per cent excess) in 10 ml water was treated with 1 g iodine dissolved in 25 ml ether. The layers were separated, and the ether solution treated with a few centigrams $(\text{iso-C}_4\text{H}_9\text{O})_2\text{OPSK}$ in 2 ml water. Now colourless, it was dried, and the product isolated as described p. 25.

0.1022 g subst.: 0.1065 g BaSO_4 . 0.09938 g subst.: 24.51 ml 0.5037 *N* NaOH.

$((\text{C}_4\text{H}_9\text{O})_2\text{OPS})_2$ (450.5) Calc. P 13.8 S 14.2
Found » 13.7 » 14.3

(4) 1 g $((\text{CH}_3\text{O})_2\text{OPS})_2$ dissolved in 10 ml water was added to 10 ml water containing

(a) 3.4 g $(\text{iso-C}_3\text{H}_7\text{O})_2\text{OPSK}$ (100 % excess)

(b) 2.1 g $(\text{iso-C}_4\text{H}_9\text{O})_2\text{OPSK}$ (10 % excess)

(c) 2.3 g $(\text{iso-C}_5\text{H}_{11}\text{O})_2\text{OPSK}$ (10 % excess).

In all three cases a colourless oil immediately separated out and gathered on the bottom of the flask. Ether was added, and the products isolated as described p. 25.

0.06215 g subst.: 17.49 ml 0.5037 *N* NaOH. 0.1089 g subst.: 0.1287 g BaSO_4 .

$((\text{C}_3\text{H}_7\text{O})_2\text{OPS})_2$ (394.4) Calc. P 15.7 S 16.3
Found » 15.7 » 16.2

0.09581 g subst.: 23.83 ml 0.5037 *N* NaOH. 0.1073 g subst.: 0.1123 g BaSO_4 .

$((\text{C}_4\text{H}_9\text{O})_2\text{OPS})_2$ (450.5) Calc. P 13.8 S 14.2
Found » 13.8 » 14.4

0.08334 g subst.: 18.31 ml 0.5037 *N* NaOH. 0.1139 g subst.: 0.1060 g BaSO_4 .

$((\text{C}_5\text{H}_{11}\text{O})_2\text{OPS})_2$ (506.6) Calc. P 12.2 S 12.7
Found » 12.2 » 12.8

Indicator reactions. To 2 ml 0.005 *M* $((\text{CH}_3\text{O})_2\text{OPS})_2$ and $((\text{C}_2\text{H}_5\text{O})_2\text{OPS})_2$, respectively, in acetonitril (previously distilled over phosphorus pentoxide) were added 2 ml *assym. bis-(p-dimethylaminophenyl)-ethylene* (one part per thousand) in the same solvent. In a few seconds a blue colour developed. The colour rapidly faded as 4 ml 0.01 *M* piperidinium *cyclo-pentamethylenedithiocarbamate* (in acetonitril) were added.

The reaction with p-toluenesulphinate. To 1 g $((\text{CH}_3\text{O})_2\text{OPS})_2$ in 10 ml water was added 1 g $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{Na} \cdot 2\text{H}_2\text{O}$ (32 per cent excess) in 10 ml water. A semi-solid liquid at once separated out, which further solidified on boiling. Yield 0.68 g (theor. 0.65 g $(p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{S})_2$). It was recrystallized from glacial acetic acid, 0.31 g dry product being obtained. Colourless crystals, m. p. 184°C , with the typical tetragonal pyramidal appearance⁵ of monosulphur di- $(p\text{-toluenethiosulphonate})$. 0.06113 g subst.: 0.1753 g BaSO_4 . $\text{S}(\text{S}_2\text{O}_2\text{C}_7\text{H}_7)_2 = 406.6$. Calc. S 39.4. Found S 39.4. The mother liquor presumably contained the corresponding trithionic compound, however, no definite products could be isolated.

Dialkylselenophosphatogens

(1) To 5 g $(\text{CH}_3\text{O})_2\text{OPSeNa}$ in 5 ml water were added 2 g iodine dissolved in 50 ml ether. On stirring, the aqueous and the ethereal layer assumed a brown and a brownish-green colour, respectively. The two layers were separated, and the aqueous layer extracted twice with 25 ml ether. The ether solutions were mixed, thoroughly dried over anhydrous sodium sulphate, and the ether evaporated off *in vacuo* until about 20 ml were left. On cooling in a carbon dioxide-acetone freezing mixture pale greenish crystals separated. The mother liquor was decanted, and the crystals treated twice with cold petrol ether. They were then transferred by means of a cooled metal spatula into a small tube-shaped vacuum exsiccator kept in a carbon dioxide-acetone freezing mixture, and the exsiccator was evacuated. Its lower part contained some phosphorus pentoxide and solid paraffine. The melting point was determined as follows: A metal thread was fixed round the mercury bulb of a short thermometer, and the thermometer cooled to -10°C in a transparent tube-shaped vacuum exsiccator containing some phosphorus pentoxide. Some crystals were placed on the thermometer bulb (the metal thread preventing their falling off), and the thermometer replaced in the exsiccator, which was evacuated. The temperature was allowed to rise through removing the exsiccator from the freezing mixture, and the temperature recorded at which the crystals liquified. M. p. $3-4^\circ\text{C}$ (corr.).

Selenium and phosphorus analyses were made as described pp. 16—17.

0.2815 g subst.: 0.1183 g Se, 5 · 17.23 ml 0.4845 N NaOH.

$((\text{CH}_3\text{O})_2\text{OPSe})_2$ (376.0) Calc. Se 42.0 P 16.5
Found » 42.0 » 16.4

An 0.005 M aqueous solution liberated selenium (red) after 10 minutes. 10 ml to which had been added 1 ml 0.01 M $p\text{-toluenesulphinate}$ became red after about 1 minute.

(2) To 5 g $(\text{C}_2\text{H}_5\text{O})_2\text{OPSeK}$ in 5 ml water were added 2 g iodine in 50 ml ether, and the mixture was agitated for some minutes. The aqueous layer remained colourless, evidently due to the smaller solubility in water and higher solubility in ether of the ethyl compound as compared with the methyl compound. The ethereal layer was treated in the usual way. The residual oil did not crystallize even when cooled to -70°C .

0.4095 g subst.: 0.1496 g Se, 5 · 22.28 ml 0.4845 N NaOH.

$((\text{C}_2\text{H}_5\text{O})_2\text{OPSe})_2$ (432.1) Calc. Se 36.6 P 14.4
Found » 36.5 » 14.6

- (3) 1 g $((\text{CH}_3\text{O})_2\text{OPSe})_2$ dissolved in 20 ml water was added to 10 ml water containing
 (a) 1.8 g $(\text{iso-C}_4\text{H}_9\text{O})_2\text{OPSeK}$ (10 per cent excess)
 (b) 2.0 g $(\text{iso-C}_5\text{H}_{11}\text{O})_2\text{OPSeK}$ (10 per cent excess).

In both cases brownish green oils immediately separated. Ether was added, and the products isolated as described p. 25.

0.4407 g subst.: 0.1266 g Se, 5 · 18.17 ml 0.5037 N NaOH.

$((\text{C}_4\text{H}_9\text{O})_2\text{OPSe})_2$ (544.3) Calc. Se 29.0 P 11.4
 Found » 28.7 » 11.5

0.4389 g subst.: 0.1153 g Se, 5 · 16.21 ml 0.5037 N NaOH.

$((\text{C}_5\text{H}_{11}\text{O})_2\text{OPSe})_2$ (600.4) Calc. Se 26.3 P 10.3
 Found » 26.3 , 10.3

- (4) 2 g $((\text{C}_2\text{H}_5\text{O})_2\text{OPS})_2$ in 25 ml ether were treated with 3.1 g $(\text{C}_2\text{H}_5\text{O})_2\text{OPSeNa}$ (10 per cent excess) in 10 ml water. The ethereal layer rapidly assumed a brownish green colour. The layers were separated, and the product isolated as described p. 25.

0.4323 g subst.: 0.1576 g Se, 5 · 22.26 ml 0.5037 N NaOH.

$((\text{C}_2\text{H}_5\text{O})_2\text{OPSe})_2$ (432.1) Calc. Se 36.6 P 14.4
 Found » 36.5 » 14.3

- (5) 2 g $((\text{iso-C}_3\text{H}_7\text{O})_2\text{OPS})_2$ in 25 ml ether were treated with 3.2 g $(\text{iso-C}_3\text{H}_7\text{O})_2\text{OPSeK}$ (10 per cent excess) in 10 ml water.

The reaction took place and the product was isolated as in (4).

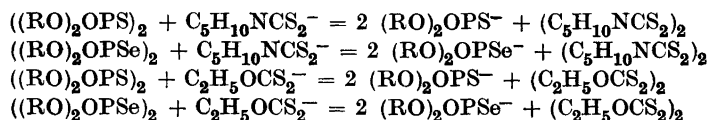
0.4166 g subst.: 0.1343 g Se, 5 · 18.85 ml 0.5037 N NaOH.

$((\text{C}_3\text{H}_7\text{O})_2\text{OPSe})_2$ (488.2) Calc. Se 32.3 P 12.7
 Found » 32.2 » 12.6

Solutions of dialkylselenophosphatogens in ether are rapidly decoloured by the action of aqueous sodium thiosulphate. Also piperidine causes a rapid fading of the colour.

The reactions of dialkylthiophosphatogens and dialkylselenophosphatogens with thiocarbonyl salts

The methyl and ethyl compounds were brought into reaction with piperidinium *cyclo*-pentamethylenedithiocarbamate, the *iso*-amyl compounds with potassium ethyl-xanthate:



1. To 25 ml 0.22 M aqueous $[\text{C}_5\text{H}_{10}\text{NCS}_2]$ $[\text{C}_5\text{H}_{10}\text{NH}_2]$ (1.35 g) in a beaker provided with a mechanical stirrer were added 0.0025 mole phosphatogen, dissolved in water. The reaction product rapidly separated out as voluminous crystals. They were filtered

off, dried, and recrystallized from alcohol. The melting point of *cyclo*-pentamethylene-thiocarbamyldisulphide is 130° C.⁴⁵

- (a) 0.71 g ((CH₃O)₂OPS)₂ (in 25 ml water) yielded 0.78 g crude product (theor. 0.81 g). M. p. (recrystallized) 130° C.
 (b) 0.84 g ((C₂H₅O)₂OPS)₂ (in 100 ml water) yielded 0.80 g crude product (theor. 0.80 g). M. p. (recrystallized) 131° C.
 (c) 0.84 g ((CH₃O)₂OPSe)₂ (in 25 ml water) yielded 0.68 g crude product (theor. 0.72 g). M. p. (recrystallized) 130° C.
 (d) 0.99 g ((C₂H₅O)₂OPSe)₂ (in 100 ml water) yielded 0.73 g crude product (theor. 0.74 g). M. p. (recrystallized) 129—130° C.

2. 25 ml 0.22 M aqueous C₂H₅OCS₂K (0.88 g) were treated for some minutes with 0.0025 mole phosphatogen dissolved in 25 ml ether. The layers were separated, the ethereal layer dried over anhydrous sodium sulphate, and the ether evaporated off *in vacuo*. The residual crystals were recrystallized from alcohol. The melting point of ethylxanthyl-disulphide is 32.5° C.¹⁰

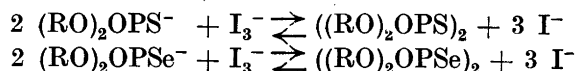
- (a) 1.26 g ((*iso*-C₅H₁₁O)₂OPS)₂. M. p. of product 31° C.
 0.03388 g subst.: 0.1302 g BaSO₄.
 (C₂H₅OCS₂)₂ = 242.4. Calc. S 52.9. Found S 52.8.
 (b) 1.50 g ((*iso*-C₅H₁₁O)₂OPSe)₂. M. p. of product 31—32° C.
 0.03008 g subst.: 0.1157 g BaSO₄. Found S 52.8.

SUMMARY

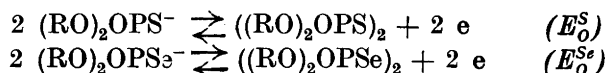
A new method has been worked out for the preparation of di-O-alkylmonothiophosphates and di-O-alkylmonoselenophosphates, *viz.*, by adding sulphur or selenium to the corresponding sodium or potassium phosphites in alcohol-ether solution.

Iodometric methods are described for the analysis of the salts.

The equilibria

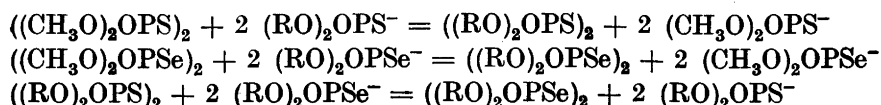


have been investigated in aqueous solutions, and the redox potentials of the systems



calculated from the obtained equilibrium constants. The potentials, in dependence of the nature of the alkyl groups, decrease in the order methyl, ethyl, *n*-propyl, primary butyl, *iso*-propyl, *sec*-butyl, and primary amyl compounds.

The pseudohalogens $((\text{RO})_2\text{OPS})_2$ and $((\text{RO})_2\text{OPSe})_2$ are prepared, and their properties studied. Reactions are demonstrated, of the type:



The theoretical degrees of reaction are calculated from the redox potentials E_0^S and E_0^{Se} .

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