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Organic Monothiopyrophosphates

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The present state of the chemistry of organic monothiopyrophosphates is described. Discussion of methods of preparation is followed by consideration of physical and chemical properties. Close attention is paid to symmetrical monothiopyrophosphates and their isomerisation, as well as the properties distinguishing them from the unsymmetrical isomers. A list of 72 references is included.

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I. INTRODUCTION

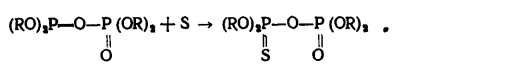
Isomeric monothiopyrophosphoric acids $H_4P_2O_6S$, in contrast to pyrophosphoric (diphosphoric) acid $H_4P_2O_7$, are unknown in the free state. However, their esters are known, as well as structural analogues containing a direct carbon–phosphorus bond. The present Review covers the chemistry of monothiopyrophosphoric esters, in whose molecules the sulphur atom is located either symmetrically or unsymmetrically



which we shall term symmetrical or unsymmetrical monothiopyrophosphates. Such compounds merit special attention because of the diversity of their chemical reactions and their great practical value. They are also of theoretical interest. An existing review[1] covering the development of the chemistry of organic monothiopyrophosphates has already become insufficiently exhaustive.

II. METHODS OF PREPARATION

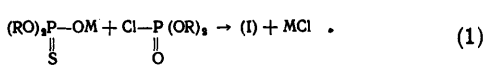
Tetraethyl thiopyrophosphate was first obtained in 1931 by A.E. and B.A.Arbuzov[2], by the addition of sulphur to the mixed anhydride of diethyl hydrogen phosphite and diethyl hydrogen phosphate:



R=Et (I)

An unsymmetrical structure was ascribed to compound (I).

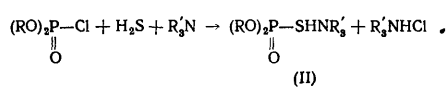
Many fresh attempts to prepare monothiopyrophosphates began two decades later. A large group of methods developed earlier were based on the phosphorylation, usually by means of dialkyl phosphorochloridates, of inorganic and organic salts of dialkyl phosphorothionates[3-6]:



(1)

The reactions are conducted with the sodium, potassium, and ammonium salts in aprotic solvents. The method was modified[7] to effect more convenient isolation of the final product.

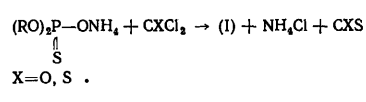
The formation of monothiopyrophosphates by the action of hydrogen sulphide on dialkyl phosphorochloridates in the presence of bases[8,9] can be regarded as a two-stage process. In the rate-determining first stage a salt of dialkyl hydrogen phosphorothionate (II) appears:



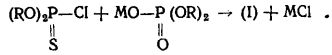
(II)

In the second stage this salt (II) undergoes phosphorylation as in Eqn. (1).

Tetra-alkyl thiopyrophosphates (I) were obtained by the action of carbonyl or thiocarbonyl chloride on ammonium dialkyl phosphorothionates[1,10-12]:

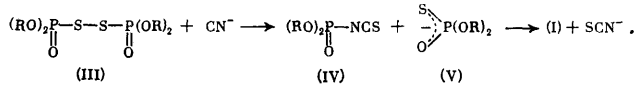


The mechanism of this reaction has not yet been adequately elucidated. An analogous method is based on the thiophosphorylation of dialkyl hydrogen phosphates or their salts[9]:



This reaction provides indirect evidence of the unsymmetrical structure of (I).

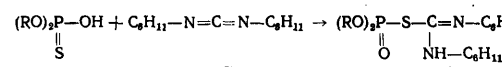
The reaction between the diphosphoryl disulphides (III) and potassium cyanide requires separate discussion[13]. These disulphides (III) are readily formed by the oxidation of salts of dialkyl hydrogen phosphorothioates[14], so that this method has preparative value. Investigations in our laboratory[15] on the preparation and chemistry of organophosphorus thiocyanates indicate a two-stage reaction:



(III) (IV) (V)

The extremely unstable intermediate thiocyanate is converted into the isothiocyanate (IV), which then reacts with the dialkyl phosphorothioate anion (V) formed at the same time. An analogy is clearly evident between this reaction and the phosphorylation of phosphorothioic acids in conformity with Eqn. (1).

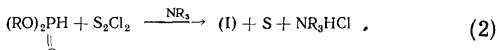
The condensation of dialkyl hydrogen phosphates with dicyclohexylcarbodi-imide (VI) [9] is the same type of reaction. It involves initial formation of the intermediate adduct (VII):[16]



(VI) (VII)

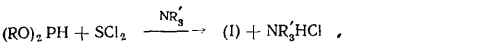
In the second stage this adduct (VII) phosphorylates another molecule of the phosphorothioate.

Two additional methods for obtaining tetra-alkyl thiopyrophosphates must be mentioned. The first is based on reaction between a dialkyl phosphite and sulphur monochloride in the presence of an amine[17-19]:



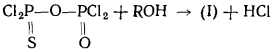
(2)

The final product is isolated from the reaction mixture by distillation. In the second method sulphur dichloride is used in the presence of a tertiary amine[18-23]:



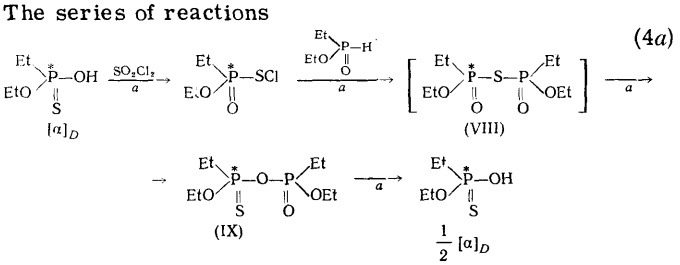
(3)

The dichloride and the amine can be replaced by the dialkylaminosulphenyl chloride R'_2NSCl.[20,21] Present-day knowledge indicates that the primary product of reaction (2) is the diphosphoryl disulphide (III), which breaks down with formation of an unsymmetrical thiopyrophosphate[24]. Reaction (3) involves initial formation of a symmetrical thiopyrophosphate, which in the presence of the amine and at a higher temperature is converted into an unsymmetrical isomer. A special method for obtaining an unsymmetrical thiopyrophosphate, in which the PS.O.PO group of the initial product remains undisturbed, is alcoholysis of thiopyrophosphoric tetrachloride[25]:



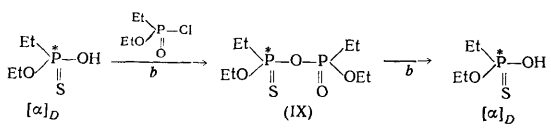
which is accompanied by alcoholysis of the P–O–P bond.

Thermochemical estimates indicate that in thiopyrophosphates the unsymmetrical skeleton is more stable than the symmetrical skeleton by ~35 kJ mole^{-1}.[26] This suggested that thiopyrophosphates containing a P–S–P group should be sufficiently stable to be isolated. In 1962 application of a stereochemical method proved[27,28] that an intermediate product containing this group is formed in the reaction between an optically active chlorothio-alkylphosphinic ester and an alkylphosphinic ester. The series of reactions



(4*a*)

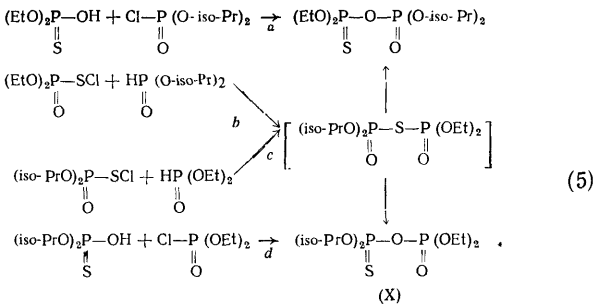
leads to half the optical activity of the initial phosphonothioic ester. Such an experimental result can be explained only by formation of the symmetrical bond system (O)P–S–P(O) in the intermediate product (VIII), which is then converted into the product (IX). This conclusion is supported by the series of reactions



(4*b*)

which results in hardly any change in the optical activity of the substrate.

Proof of the intermediate formation of a symmetrical thiopyrophosphate was obtained by investigating the reactions of dialkyl *S*-chlorothiophosphonates with dialkyl phosphites[29]

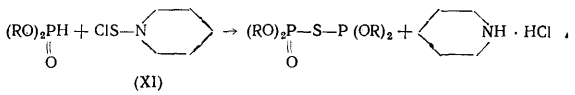


(5)

(X)

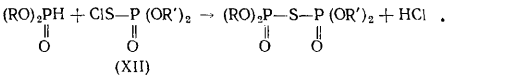
The final product of reactions (5*b*) and (5*c*) is always an unsymmetrical thiopyrophosphate (X). This provides convincing support for the view that reactions (5*a*) and (5*d*)—the phosphorylation of dialkyl hydrogen phosphorothioates by means of dialkyl phosphorochloridates according to scheme (1)—leads directly to the formation of a P–O–P bond without intermediate formation of a product having a symmetrical skeleton.

It was subsequently established[23] that symmetrical thiopyrophosphates are formed in the reaction of a dialkyl *S*-chlorothiophosphonate with a dialkyl phosphite[23]. A general method was the reaction of dialkyl phosphites with piperidinosulphenyl chloride (XI),[23,30] yielding symmetrical thiopyrophosphates containing four identical substituents:



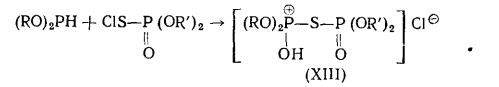
(XI)

A more general method is use of the dialkyl *S*-chlorothiophosphonate (XII),[31,32] which enables different substituents to be attached to the different phosphorus atoms:



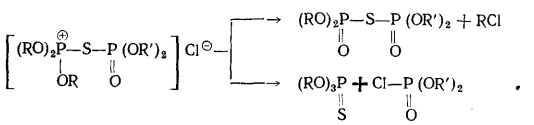
(XII)

These reactions are probably of the Arbuzov type[28,30-32] with formation of an intermediate phosphonium complex:



(XIII)

This complex (XIII) breaks down to form a symmetrical thiopyrophosphate and hydrogen chloride. The use of trialkyl phosphites $(RO)_3P$ instead of dialkyl phosphites $(RO)_2POH$ may change the mode of decomposition of the complex (XIV):[31]

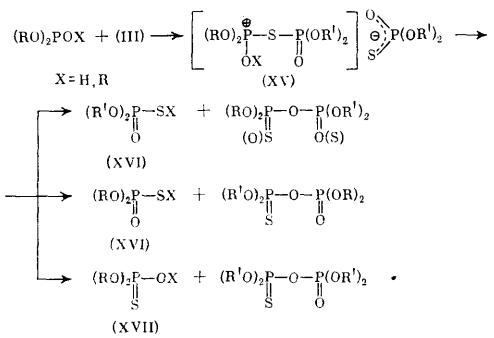


(XIV)

In such a case the symmetrical thiopyrophosphate is accompanied by the corresponding trialkyl phosphorothionate and dialkyl phosphorochloridate.

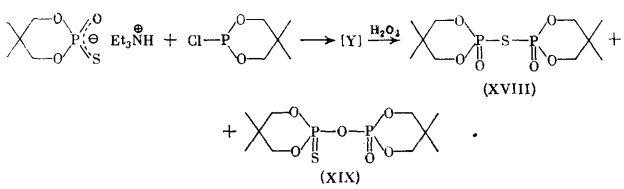
A special group of reactions for obtaining monothiopyrophosphates involve the diphosphoryl disulphides (III) with dialkyl[33,34] or trialkyl[35] phosphites. At present it is thought most probably that the reaction mechanism

involves intermediate formation of a phosphonium complex (XV):



If in (XV) the substituent X = H, the cation of the complex (XV) is identical with the cation of the compound, and decomposition of (XV) yields a symmetrical thiopyrophosphate. If X = Alk, the cation (XV) contains three electrophilic centres—the substituent X and the two phosphorus atoms—with the occurrence of three parallel substitutions by an anion, since dialkylation of the cation (XV) is slower than deprotonation of the cation (XIII). The substitution products when X is an alkyl group are a trialkyl phosphorothioate (XVI) and two isomeric unsymmetrical thiopyrophosphates formed by isomerisation of the symmetrical skeleton. Two other reactions result from substitution by an anion at the two phosphorus atoms: substitution at the phosphonium atom P^+ yields a trialkyl phosphorothiolate (XVI) and an unsymmetrical thiopyrophosphate, whereas substitution at the phosphorus atom of the phosphinyl group leads to formation of a trialkyl phosphorothionate (XVII) and an unsymmetrical thiopyrophosphate containing four identical substituents. The action of triphenylphosphine on di(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinan-2-yl) disulphide follows a similar course[36] to give an unsymmetrical thiopyrophosphate and a dithiopyrophosphate.

The first stable symmetrical monothiopyrophosphate to be synthesised was di-5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinan-2-yl sulphide (XVIII), obtained from an ammonium phosphorothioate and a phosphorochloridite[37]:



Three isomeric structures—essentially PO.S.P, PO.PS, and PS.O.P—can be suggested[38] for the unidentified unstable product Y obtained in the first stage. Oxidation of Y directly after formation gives a symmetrical thiopyrophosphate (XVIII), whereas oxidation of Y after storage yields an unsymmetrical thiopyrophosphate (XIX). The original attempts to obtain symmetrical thiopyrophosphates by oxidising compounds containing a P.S.P group always resulted in an unsymmetrical isomer[39,40].

Methods for obtaining thiopyrophosphates can in general be divided into two groups, comprising those leading directly to unsymmetrical products and those in which symmetrical thiopyrophosphates are formed, at least as intermediate products. The phosphorylation of dialkyl hydrogen phosphorothioates and the thiophosphorylation of dialkyl hydrogen phosphates by compounds such as dialkyl phosphorochloridates belong to the first group. The first or second substrate is often an intermediate formed in the reaction medium. In our view several published methods yielding thiopyrophosphates, whose mechanisms have not yet been fully investigated[18,41-45], can also be included in this group. The second group is based on the reactions of dialkyl phosphites with sulphenyl compounds. They involve an intermediate phosphonium complex and yield symmetrical thiopyrophosphates, but it is often impossible to isolate the latter from the reaction medium[18-22,31,46-49] owing to isomerisation. The presence of amines, acids, or ammonium salts, as well as an incorrect purification technique, results in rapid conversion of symmetrical into unsymmetrical products. These facts make clear why symmetrical thiopyrophosphates were exclusively obtained in much of the earlier work. Formally, the isomerisation of symmetrical into unsymmetrical thiopyrophosphates can be regarded as an effective method for obtaining the latter.

III. STRUCTURE AND PHYSICAL PROPERTIES

Tetra-alkyl monothiopyrophosphates are oily, non-volatile liquids, readily soluble in organic solvents but sparingly soluble in water. Several of them, e.g. derivatives of neopentyl glycol and alcohol, are crystalline.

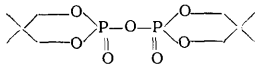
The intense biological activity of unsymmetrical thiopyrophosphates has been known for a long time: they are poisons, blocking the choline esterase system[50,51]. In view of the strong phosphorylating properties of symmetrical thiopyrophosphates, they may also be expected to possess high biological activity. Caution must be exercised in working with thiopyrophosphates.

Spectral and several other properties of monothiopyrophosphates have been reported[30-32], among which the infrared and phosphorus-31 nuclear magnetic resonance spectra are most characteristic. The infrared spectra of symmetrical thiopyrophosphates contain an absorption band in the range 520–545 cm^{-1}, corresponding to vibrations of P–S–P bonds. The characteristic band of the P=O group appears at 1270–1315 cm^{-1}, at lower wavenumbers for symmetrical thiopyrophosphates. Bands due to the P=S and P–O–P groups in unsymmetrical thiopyrophosphates are less intense, and usually appear in the region of deformation vibrations of the bonds of alkyl substituents.

As can be predicted, the signals of phosphorus nuclei in the ^{31}P n.m.r. spectrum of monothiopyrophosphates have the form, after the spin interaction of phosphorus and hydrogen nuclei has been decoupled, of pairs of separate singlets. The spectra of symmetrical thiopyrophosphates having four identical substituents contain ^{31}P n.m.r. singlet signals. The chemical shift relative to orthophosphoric acid of the phosphoryl group in symmetrical thiopyrophosphates lies between −15 and −5 ppm. In the spectra of unsymmetrical thiopyrophosphates the chemical shifts of phosphoryl and thiophosphoryl groups are respectively +12–25 and −55 to −40 ppm.[52,53]

Infrared[9,54] and Raman[55] spectra have been used to confirm unsymmetrical structures. At the present time the most convenient method of structure investigation and identification of thiopyrophosphates is ^{31}P supplemented by ^{1}H n.m.r. spectroscopy. Recently, unsymmetrical tetraethyl monothiopyrophosphate has been used to investigate the structure of organic compounds by means of the Faraday effect[56].

Table 1 lists results of the X-ray examination of the lattice structure[57] of the cyclically substituted monothiopyrophosphates (XVIII) and (XIX) together with the analogous cyclic pyrophosphate.



(XX)

Table 1. Crystallographic data for 2,2-dimethyltrimethylene pyrophosphate and monothiopyrophosphates[57].

Ester	Space group	Parameters of unit cell				X-ray density, g cm^{-3}
		No. of mol.	lattice constants, A			
			a	*b*	*c*	
(XVIII)	*Pbca*	4	18.66	9.25	9.05	1.40
(XIX)	*Pbca*	8	27.96	9.84	11.28	1.41
(XX)	*Pbca*	8	26.90	10.00	11.13	1.39

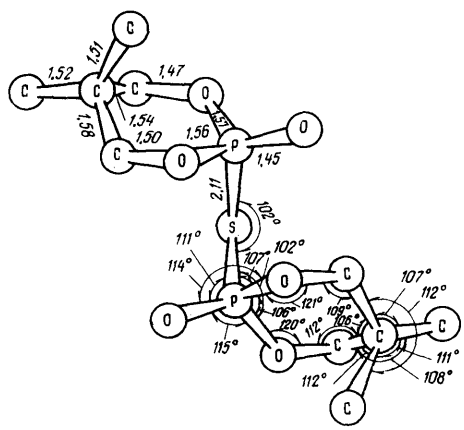


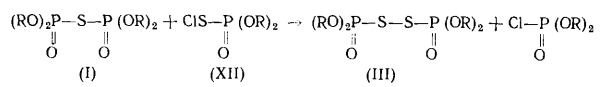
Figure 1. Structure of a molecule of symmetrical bis-2,2-dimethyltrimethylene thiopyrophosphate (XVIII) in the crystal.

The unsymmetrical thiopyrophosphate (XIX) and the pyrophosphate form isostructural crystals in the form of rhombic bipyramids. The symmetrical thiopyrophosphate (XVIII) also has a rhombic lattice, but with different symmetry and unit cell parameters. The molecule of (XVIII), who structure in the crystal[58] is illustrated in Fig. 1, differs from the pyrophosphate[59] and the unsymmetrical thiopyrophosphate in having a twofold symmetry axis lying in the plane of the P–S–P bond system and passing through the central sulphur atom. It is characterised by long P–S bonds and relatively remote oxygen atoms in the P=O groups. The dioxaphosphan rings are flatter than the cyclohexane ring. Such flattening is exhibited by other dioxaphosphans[59,60]. The central sulphur atom in this symmetrical molecule, like the central oxygen atom in the pyrophosphate, occurs in the crystal in an axial position[58,59] with respect to the principal plane of the dioxaphosphan rings. In solution this molecular structure of (XVIII) is probably atypical, since the ^{1}H n.m.r. spectra of solutions indicate an equatorial arrangement[61] of the sulphur atom.

IV. CHEMICAL PROPERTIES

Tetra-alkyl monothiopyrophosphates contain three types of reactive centres—electrophilic phosphorus and carbon atoms and the nucleophilic sulphur atom—so that this group of compounds is characterised by three types of reactions. The chemical properties of organic monothiopyrophosphates are determined mainly by the presence around the phosphorus atoms of two strong electrophilic centres and "good" leaving groups. In this sense thiopyrophosphates resemble their oxygen analogues—pyrophosphates.

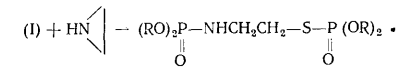
Examples of reactions in which nucleophilic properties are developed are that of an unsymmetrical thiopyrophosphate with elementary chlorine, giving a mixture of products containing the P–SCl group, and the slow reaction of a symmetrical thiopyrophosphate with the dialkyl *S*-chlorothiophosphonate (XII), yielding the diphosphoryl disulphide (III) [32]



(I) (XII) (III)

Alkylating properties may appear at the carbon atoms of a thiopyrophosphate during nucleophilic substitution. Such reactions have not been investigated systematically, but after an unsymmetrical thiopyrophosphate has been stored or heated the corresponding phosphates, thiophosphates, and polymeric products are detected[9].

The addition of aziridine to the P–S–P chain in thiopyrophosphates, yielding diphosphorylated derivatives of 2-aminoethanethiol, has recently been described in the patent literature[62]. In the case of a symmetrical thiopyrophosphate the course of the reaction is



The first stage probably involves nucleophilic substitution at the phosphorus atom; after this the anion of phosphorothioic acid adds to the aziridine residue.

From the difference in energy between the O–P and S–P bonds in the thiopyrophosphate skeletons[26,63] we may predict that symmetrical isomers will react more vigorously than unsymmetrical isomers in reactions of a phosphoryl centre with nucleophilic compounds. This represents an interesting case of the presence of a leaving group, which is a "better" group not only because of the stability of the anion formed but also because the energy of the ruptured bond is less.

In symmetrical monothiopyrophosphates two phosphoryl groups are the reaction centres. Their relative reactivity depends solely on the nature of the substituents attached to the phosphorus atom. The unsymmetrical isomers contain two different groups—phosphoryl and thiophosphoryl—of which the former undergoes nucleophilic substitution more rapidly[37,64]. Reaction on the latter centre can be observed provided that the reactivity of the former is diminished by appropriate choice of substituents; such diminution may be accomplished also by the type of nucleophilic reagent employed[65].

An unsymmetrical thiopyrophosphate undergoes hydrolysis almost exclusively at the phosphoryl centre. Kinetic data[66] for the hydrolysis of tetraethyl pyrophosphate and the corresponding unsymmetrical thiopyrophosphate indicate that the presence of the sulphur atom in the latter has relatively little effect on the reactivity of the phosphoryl centre (Table 2). Comparison of kinetic results for the hydrolysis of mono- and di-thiopyrophosphates[67,68] confirm (Table 2) the lower reactivity of the thiophosphates found with trisubstituted phosphates and phosphorothioates[69,70].

Table 2. Rates of hydrolysis of tetraethyl pyrophosphate, unsymmetrical thiopyrophosphate, and dithiopyrophosphate.

Compound	Aqueous solvent (dioxan, %)	Hydrolysis rate const. 10^5k, s^{-1}	Arrhenius activation parameters		Ref.
			E, kJ mole^{-1}	lg A	
$(EtO)_2P(O)-O-P(O)(OEt)_2$	0	41.0*	44.0	3.12	66
$(EtO)_2P(S)-O-P(O)(OEt)_2$	0	21.8	51.9	4.02	66
	50	2.53	67.8	5.43	67
$(EtO)_2P(S)-O-P(S)(OEt)_2$	50	0.85	116.9	12.18	68

* Calculated by means of the Arrhenius equation.

Table 3. Kinetic data for the alkaline and acid hydrolysis of unsymmetrical tetraethyl monothiopyrophosphate at 25°C.[66]

Solvent	$10^5 k$	Arrhenius activation parameters	
		E, kJ mole^{-1}	lg A
Water	0.82 s^{-1}	51.9	4.02
KOH, 0.02 M	9600 M^{-1} s^{-1}	50.6	7.86
HCl, 5.78 M	1.19 s^{-1}	75.8	8.35

Hydrolysis of tetraethyl monothiopyrophosphate is considerably more rapid in alkaline than in neutral medium, while the catalytic effect of acids is insignificant. Table 3 gives some kinetic data for this process. The mechanism of the reaction is explained on the basis of specific acid–base catalysis.

The reactivities of symmetrical and unsymmetrical thiopyrophosphates have been compared[71] with respect to neutral hydrolysis in aqueous dioxan solution with the cyclic compounds (XVIII) and (XIX) as examples. The two compounds yield identical organic phosphoric and phosphorothioic acids as hydrolysis products. The rate of reaction of the symmetrical isomer exceeds that of the unsymmetrical isomer approximately hundredfold (Table 4). The reaction velocity is influenced significantly by solvation[67,71], whose role is indicated by a difference for these isomers in the dependence of the hydrolysis rate constant on the dioxan content of the solvent (Fig. 2).

An interesting reaction is the nucleophilic substitution of a symmetrical thiopyrophosphate by the dialkyl phosphorothioate anion[32], in which an unsymmetrical isomer is formed with regeneration of the nucleophilic reagent:

$$(I) + {}^{\ominus}O-P(S)(OR')_2 \rightarrow (RO)_2P(O^{\ominus})=S + (RO)_2P(S)-O-P(O)(OR')_2 .$$

Table 4. Rates of hydrolysis of symmetrical and unsymmetrical thiopyrophosphates in aqueous dioxan at 80°C.[71]

Compound	Dioxan mole fraction	$10^5 k$, s^{-1}	Arrhenius activation parameters		Compound	Dioxan mole fraction	$10^5 k$, s^{-1}	Arrhenius activation parameters	
			E, kJ mole^{-1}	lg A				E, kJ mole^{-1}	lg A
(XVIII)	0.2	103*	66.5	6.89	(XIX)	0.2	0.52	69.1	5.05
(XVIII)	0.6	17*	58.2	4.84	(XIX)	0.6	0.072	71.2	8.33

* Calculated by means of the Arrhenius equation.

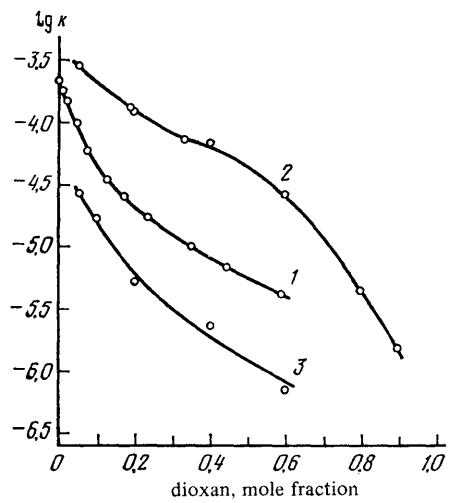
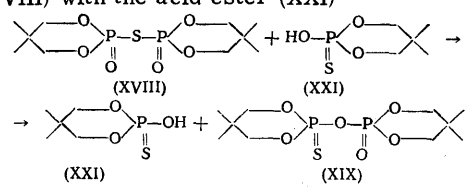


Figure 2. Dependence of hydrolysis rate constant on mole fraction of dioxan in aqueous solvent: 1) unsymmetrical tetraethyl thiopyrophosphate (80°C);[67] 2) symmetrical thiopyrophosphate (XVIII) (50°C);[71] 3) unsymmetrical thiopyrophosphate (XIX) (80°C).[71]

The reaction is bimolecular, but if the two reagents have the same substituents (R = R') the reaction velocity is described by a first-order kinetic equation. Activation parameters for the reaction of the symmetrical thiopyrophosphate (XVIII) with the acid ester (XXI)[72]



have been determined as $\Delta H^{\neq} = 69$ kJ mole^{-1} and $S^{\neq} = -74$ J mole^{-1} deg^{-1}. The reaction is accelerated in the presence of amines. The above reactions most probably occur when contaminated specimens of symmetrical thiopyrophosphates are stored, and lead to spontaneous isomerisation of the latter.

The thermal isomerisation of a symmetrical thiopyrophosphate, which may proceed in parallel with the above reaction with an organic phosphorothioic acid, is unimolecular. The thermodynamic parameters of this reaction have been determined for the symmetrical (XVIII) in a polar solvent as $\Delta H^{\neq} = 128$ kJ mole^{-1} and $\Delta S^{\neq} = -16$ J mole^{-1} deg^{-1}. The transition state is probably amphoteric in structure.

Our kinetic investigations and certain qualitative results suggest that unsymmetrical are formed from symmetrical thiopyrophosphates by two independent reactions—unimolecular thermal isomerisation and bimolecular nucleophilic substitution.

REFERENCES

1. G. Schrader, W. Lorenz, and R. Mühlmann, Angew. Chem., 70, 690 (1958).
2. A. E. Arbusov and B. A. Arbusov, J. prakt. Chem., 130, 103 (1931).
3. S. A. Hall, Adv. Chem. Ser., 1, 150 (1950).
4. G. M. Kosolapoff, US P. 2 567 154 (1951); Chem. Abs., 46, P2562 (1952).
5. B. Fiszer and J. Michalski, Roczniki Chem., 25, 514 (1951).
6. B. A. Arbuzov, P. I. Alimov, M. A. Zvereva, I. D. Neklesova, and M. A. Kudrina, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1038 (1954).
7. P. I. Alimov, M. A. Zvereva, and O. N. Fedorova, in "Khimiya i Primenenie Fosfororganicheskikh Soedinenii, Trudy I Konferentsii" (Chemistry and Application of Organophosphorus Compounds—Proceedings of the First Conference), Nauka, Moscow, 1955, p. 164.
8. B. Fiszer, J. Michalski, and J. Wieczorkowski, Roczniki Chem., 27, 482 (1953).
9. R. A. McIvor, G. D. McCarthy, and G. A. Grant, Canad. J. Chem., 34, 1819 (1956).
10. A. E. Arbuzov, B. A. Arbuzov, and N. I. Rizpolozhenskii, USSR P. 100 896 (1955); Chem. Abs., 51, P15 550.
11. J. I. G. Cadogan, J. Chem. Soc., 3067 (1961).
12. G. Schrader, BRD P. 953 795 (1955); Chem. Zentr., 10 596 (1957).
13. R. Mühlmann and G. Schrader, BRD P. 947 366 (1956); Chem. Abs., 51, 4413 (1957).
14. O. Foss, Acta Chem. Scand., 1, 8 (1947).
15. A. Lopusinski, J. Michalski, and W. Stec, Annalen, 924 (1977).
16. M. Mikolajczyk, Chem. Ber., 99, 2083 (1966).
17. D. Harman and A. R. Stiles, US P. 2 630 450 (1953); Chem. Abs., 48, 7047h (1954).
18. A. E. Arbuzov, B. A. Arbuzov, P. I. Alimov, K. V. Nikonorov, N. I. Rizpolozhenskii, and O. N. Fedorova, Trudy Kazansk. Filiala Akad. Nauk SSSR, Ser. Khim. Nauk, No. 2, 7 (1956).
19. A. E. Arbuzov, B. A. Arbuzov, K. V. Nikonorov, and P. I. Alimov, USSR P. 105 897 (1957); Chem. Abs., 52, P1201 (1958).
20. W. Lorenz and G. Schrader, BRD P. 820 001 (1953); Chem. Abs., 47, 3332 (1953).
21. C. Lutter and E. Cauer, B.P. 660 833 (1951); Chem. Zentr., 3406 (1952).
22. J. Michalski and B. Pliszka, Chem. and Ind., 1052 (1962).
23. J. Michalski, M. Mikolajczyk, B. Mlotkowska, and A. Zwierzak, Angew. Chem., 79, 1069 (1967).
24. J. Michalski, M. Mikolajczyk, and A. Ratajczak, Bull. Acad. polon. Sci., Sér. Sci. chim., 11, 11 (1963).
25. E. Rother, Chem. Ber., 93, 2217 (1960).
26. R. F. Hudson, "Structure and Mechanism in Organophosphorus Chemistry", Academic Press, London, 1956, p. 123.
27. J. Michalski, M. Mikolajczyk, and A. Ratajczak, Chem. and Ind., 819 (1962).
28. J. Michalski, M. Mikolajczyk, and A. Skowronska, Chem. and Ind., 1053 (1962).
29. J. Michalski, M. Mikolajczyk, B. Mlotkowska, and A. Skowronska, Bull. Acad. polon. Sci., Sér. Sci. chim., 11, 695 (1963).
30. J. Michalski, M. Mikolajczyk, and B. Mlotkowska, Chem. Ber., 102, 90 (1969).
31. J. Michalski and A. Skowronska, J. Chem. Soc.(C), 703 (1970).
32. J. Michalski, B. Mlotkowska, and A. Skowronska, J. Chem. Soc., Perkin Trans.I, 319 (1974).
33. J. Michalski and J. Wasiak, J. Chem. Soc., 5056 (1962).
34. J. Michalski, J. Wieczorkowski, J. Wasiak, and B. Pliszka, Roczniki Chem., 33, 247 (1959).
35. J. Michalski and J. Wieczorkowski, Bull. Acad. polon. Sci., Sér. Sci. chim., 5, 917 (1957).
36. R. S. Edmundson, J. Chem. Soc. (C), 1635 (1967).
37. R. S. Edmundson, Chem. and Ind., 784 (1963).
38. V. L. Foss, Yu. A. Veits, and T. F. Lutsenko, Phosphorus Sulfur, 3, 299 (1977).
39. C. Krawiecki and J. Michalski, Chem. and Ind., 1323 (1957).
40. C. Krawiecki and J. Michalski, J. Chem. Soc., 881 (1960).
41. A. E. Arbuzov, B. A. Arbuzov, P. I. Alimov, and K. V. Nikonorov, USSR P. 105 849 (1957); Chem. Abs., 51, P15060.
42. A. G. Schering, BRD P. 1 129 156 (1959); Chem. Abs., 57, P11 021.
43. J. R. Geigy, Swiss P. 358 787 (1957); Chem. Abs., 57, P8437.
44. V. G. Pesin, A. M. Khaletskii, and I. G. Vitenberg, USSR P. 154 540 (1963); Ref. Zhur. Khim., 13N75 (1964).
45. V. G. Pesin, A. M. Khaletskii, and I. G. Vitenberg, Zhur. Obshch. Khim., 33, 388 (1963).
46. J. Michalski and B. Pliszka-Krawiecka, J. Chem. Soc. (C), 2249 (1966).
47. A. Zwierzak, Tetrahedron, 25, 5177 (1969).
48. A. Zwierzak, in "Khimiya i Primenenie Fosfororganicheskikh Soedinenii, Trudy IV Konferentsii" (Chemistry and Application of Organophosphorus Compounds—Proceedings of the Fourth Conference), Nauka, Moscow, 1972, p. 216.
49. K. A. Petrov and A. A. Neimysheva, Zhur. Obshch. Khim., 29, 3030 (1959).
50. H. C. Froede and I. B. Wilson, "The Enzymes", Edited by P. D. Boyer, Academic Press, London, 1971, Vol. 5, Part 5, p. 100.
51. G. Schrader, Z. Naturforsch., 18b, 965 (1963).
52. R. A. Y. Jones, A. R. Katritzky, and J. Michalski, Proc. Chem. Soc., 321 (1959).

53. K.D.Bartle, R.S.Edmundson, and D.W.Jones, Tetrahedron, **23**, 1701 (1967).
54. D.G.Coe, B.J.Perry, and R.K.Brown, J.Chem. Soc., 3604 (1957).
55. J.Michalski, R.Mierzecki, and E.Rurarz, Roczniki Chem., 30, 651 (1956).
56. D.Troy-Lamiere, R.Turpin, and D.Voigt, Bull. Soc.chim.France, 889 (1972).
57. M.Bukowska-Strzyzewska, Roczniki Chem., 50, 1009 (1976).
58. M.Bukowska-Strzyzewska, J.Michalski, B.Mlotkowska, and J.Skoweranda, Acta Cryst., B32, 2605 (1976).
59. M.Bukowska-Strzyzewska, and W.Dobrowolska, Acta Cryst.(in the press).
60. Mazhar-ul-Haque, C.N.Caughlan, and W.L.Moats, J.Org.Chem., 35, 1446 (1970).
61. A.R.Katritzky, J.Michalski, M.R.Nesbit, Z.Tulimowski, and A.Zwierzak, J.Chem.Soc.(B), 140 (1970).
62. R.V.Strel'tsov, L.E.Kirilina, I.I.Shinkina, and N.K.Bliznyuk, USSR P.478 835 (1973); Byull. Izobr., No.28, 58 (1975).
63. V.E.Bel'skii, N.N.Bezzubova, Z.V.Lustina, V.N.Eliseenkov, and A.N.Pudovik, Zhur.Obshch. Khim., 39, 181 (1969).
64. B.Mlotkowska, Zweszty Naukowe P.L., 27, 163 (1973).
65. B.Mlotkowska, Candidate's Thesis, Polytechnic Institute, Lódz, 1969.
66. V.E.Bel'skii, M.V.Efremova, and Z.V.Pustina, Izv.Akad.Nauk SSSR, Ser.Khim., 1236 (1967).
67. V.E.Bel'skii, M.V.Efremova, and Z.V.Lustina, Izv.Akad.Nauk SSSR, Ser.Khim., 1455 (1967).
68. V.E.Bel'skii and M.V.Efremova, Izv.Akad.Nauk SSSR, Ser.Khim., 409 (1968).
69. H.Teihmann and G.Hilgetag, Angew.Chem., 79, 1077 (1967).
70. G.Slebocka-Tilk, Candidate's Thesis, Polytechnic Institute, Lódz, 1977.
71. J.Michalski, W.Reimschüssel, and R.Kaminski, Bull.Acad.polon.Sci., Sér.Sci.chim. (in the press).
72. R.Kaminski, Candidate's Thesis, Molecular and Macromolecular Research Centre, Polish Academy of Sciences, Lódz, 1978.

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