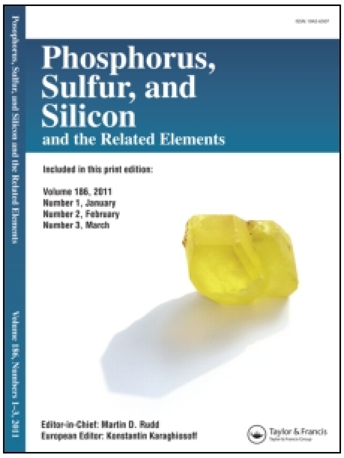

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MECHANISM OF THIONO-THIOLO ISOMERIZATION OF THIOPHOSPHATES. KINETIC EVIDENCE FOR HILGETAG'S HYPOTHESIS

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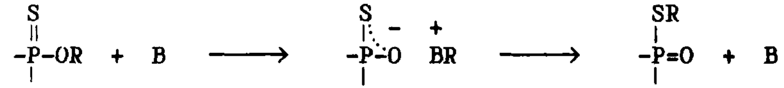
Abstract Kinetic evidence is given for Hilgetag's mechanistic conception of the thiono-thiolo isomerization of O,O-dimethyl and O-methyl thionophosphates in acetonitrile solutions containing tetramethylammonium salts with anions derived from the corresponding thionophosphates by demethylation. Some kinetic effects of reactant structures, solvents, and trimethylammonium cation of a salt are mentioned.

INTRODUCTION

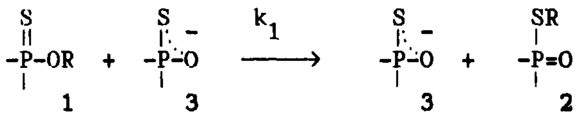
Thiono-thiolo isomerization of O-alkyl esters of phosphorus thioacids leading to corresponding S-alkyl isomers is of great importance in phosphorus chemistry and biochemistry because of wide applications of O-alkvl thiophosphates as pesticides in agriculture and nucleotide analogues in biochemical investigations. The isomerization can be effected either by Lewis and protic acids or by organic bases such as amines, phosphines and arsines. Systematic studies have permitted understanding of the reaction mechanism operating in the presence of strong protic acids[1]. For the isomerization caused by bases two mechanisms have been proposed. The first involving intramolecular realkylation[2,3] of an anion 3 by an alkylonium cation seems to operate in the case of phosphines[4] or arsines[5], and was postulated for amines[3]



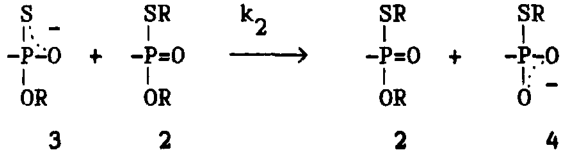
$$-\overset{\overset{S}{\|}}{\underset{|}{P}}-OR + B \longrightarrow -\overset{\overset{S}{\vdots}}{\underset{|}{P}}\overset{-}{\cdots}O \quad \overset{+}{B}R \longrightarrow -\overset{\overset{SR}{|}}{\underset{|}{P}}=O + B$$

1 3 2

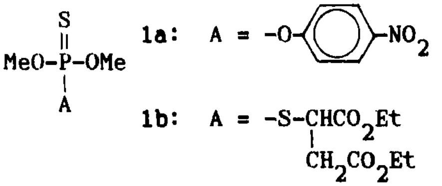
The other mechanism suggested by Hilgetag[6] for the isomerization in the presence of an alkylammonium salt involves a reaction between an anion 3 and thionoester 1 leading to the same anion and a thioloester 2

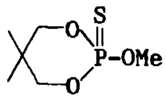


The isomerization of O,O-dialkyl thionoesters can be a kinetically complex reaction due to the anion isomerization 3 ⟶ 4 which in Hilgetag terms can be described as follows

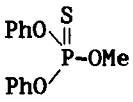


We present here some of our recent[7] results of systematic kinetic studies on the isomerization of model thionoesters **1**, both dimethyl (**1a** and **1b**) and monomethyl (**1c** and **1d**) types, in the presence of tetramethylammonium salts **3** containing the anions derived from the corresponding thionoesters **1** by demethylation. Some results of solvent effects and the effects of a trimethylammonium salt cation on reaction rates are also reported.





1c



1d

EXPERIMENTAL

Having in mind an accuracy of analytical procedure the kinetics was followed with the aid of the reactants labelled with ^{14}C in either O-methyl or S-methyl groups of the corresponding thionoesters **1**, thioloesters **2a** and **2b**, and anions **3a** and **3b**. Reagents were separated by TLC method and their radioactivities were measured by liquid scintillation technique[8]. In purified solvents (acetonitrile (AN), benzonitrile (BN), propylene carbonate (PC)) no side reactions other than expected were observed with the exception of malathion **1b** and isomalathion **2b**, the phosphorylation of which by the related anion **3b** occured but these side reactions were at least 30 times slower than the studied ones. The appropriate kinetic equations involving isotope dilution processes appearing in studied systems were solved and applied to evaluate reaction rate constants which were determined at reactant concentrations 5 - 100 mmol/l and temperatures 25 - 80°C. All statistical errors were quoted at the 0.95 confidence level. Since no direct determination of k_1 values for the reactions of **1a** with **3a** and **1b** with **3b** is possible, they were obtained from the ratio k_1/k_2 using k_2 values determined for the reaction of **2a** with **3a** and **2b** with **3b**. Activation parameters were calculated.

TABLE Second-order rate constants and activation parameters for the reactions of thionoesters **1** and thioloesters **2** with corresponding tetramethylammonium salts **3**.

Reaction and solvent			$10^4 k$ (60°C) $l\ mol^{-1} s^{-1}$	$\Delta H^{\neq}$(60°C) $kJ\ mol^{-1}$	$\Delta S^{\neq}$(60°C) $J\ mol^{-1} K^{-1}$
1a + **3a**	k_1	AN	4.82 ± 0.47	95 ± 10	-25 ± 15
2a + **3a**	k_2	AN	6.08 ± 0.30	90.0 ± 7.8	-37 ± 9
		BN	22.88 ± 1.18	87.1 ± 6.1	-50 ± 17
		PC	6.75 ± 0.42	84.8 ± 6.5	-52 ± 11
1b + **3b**	k_1	AN	1.44 ± 0.16	93 ± 12	-40 ± 25
2b + **3b**	k_2	AN	3.37 ± 0.26	87.4 ± 8.3	-50 ± 18
1c + **3c**	k_1	BN	2.54 ± 0.54	83.3 ± 2.2	-47 ± 5
1d + **3d**	k_1	BN	7.5 ± 1.2	88.6 ± 4.4	-40 ± 6
		AN	2.24 ± 0.18	87.9 ± 5.8	-55 ± 12

1d + **3d**	k_1	9.9 ± 0.4	in AN at 75,6°C.
1d + **3d(H)**	$k_{1,i}$	17.6 ± 1.2	$k_{1,i}$ and $k_{1,p}$ values evaluated from Acree equation[9] and our conductometric data.
	$k_{1,p}$	0.6 ± 0.1	

RESULTS AND DISCUSSION

Our kinetic results have completely proved Hilgetag's conception of the thiono-thiolo isomerization mechanism[6]. The isomerization of the monomethyl thionoesters studied (**1c** and **1d**) proceeds as the entirely bimolecular reaction between the ester and derivative anion (**3c** or **3d**). As in this reaction the anion acts as a catalyst, its kinetics is of the first order with the rate constant proportional to an initial concentration of the tetramethylammonium salt ($^1k_1 = {}^2k_1\ c_3^o$). The same is true for the anion isomerization reaction **3** ⟶ **4** in which the thioloester **2** plays a role of a catalyst ($^1k_2 = {}^2k_2\ c_2^0$). The kinetics of the isomerization of the dimethyl thionoester (**1a** and **1b**) in the presence of the derivative anion **3** is described by the system of two consecutive bimolecular reactions involving a competition between the thionoester and its thioloisomer **2** for the anion.

The data collected in the table for the reactions studied show some differences in the rate constants and activation parameters but they are not so strong as could be expected from the reactants structure differentiation. This feature can mean that the resultant effects of substituents at the phosphorus atoms in each pair of the reactants on the electrophilicity of the methyl ester carbon atom and the nucleophilicity of the anion sulfur atom are not only opposite but almost equal as well. On the other hand the reaction rates are quite sensitive to solvation effects as well as to the nature of a cation interacting with the anion **3**. The reaction rate constants seem to be correlated with Gutmann's acceptor number of solvents. The observed rate constant k_1 of the reaction between the thionoester **1d** and trimethylammonium salt **3d(H)** in AN solution has rapidly decreased with the increase of salt concentration but the $k_{1,i}$ value evaluated for free anions has appeared much greater than the $k_{1,p}$ value for ion pairs and also superior to the k_1 value for the same reaction proceeding with the tetramethylammonium salt. The latter feature may be explained as an autocatalytic hydrogen effect of the cation $H\overset{+}{N}Me_3$.

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