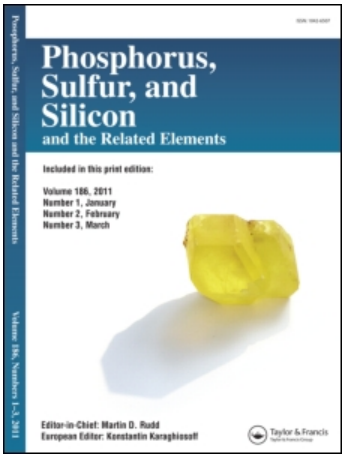

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Mechanisms of Isomerization of Sym-Monothiopyrophosphates

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MECHANISMS OF ISOMERIZATION OF SYM-MONOTHIOPYROPHOSPHATES

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Abstract The detailed mechanistic studies of the thiolo-thiono isomerization of monothiopyrophosphate 1 is presented. The application of isotopic tracers and isotopic effects kinetic methods provide evidence for two distinct mechanisms: $S_N2(P)$ reaction induced by external anionic species and the dissociative isomerization proceeding via ion pairs and ions.

The monothiopyrophosphates are structural analogues of biologically important diphosphates and play significant role in organophosphorus chemistry and stereochemistry. One of the most interesting features of their chemistry is the thiolo-thiono isomerization[1] O = P-S-P = O ⟶ S = P-O-P = O. Detailed mechanistic studies of this process were undertaken in our laboratories and some recent results are presented in this communication.

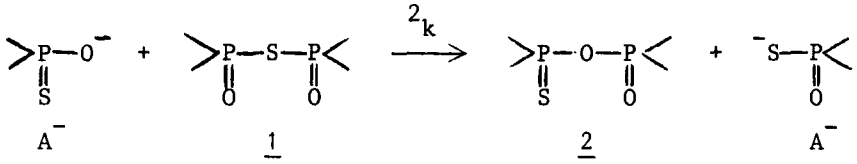
Selection of compounds suitable for mechanistic studies indicated that crystalline bis-(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinanyl) sulfide 1 is a model of choice. Having in mind the accuracy of analytical procedure we decided[2] to follow kinetics with the

1 2

aid of radioactive tracers using ^{32}P and ^{35}S nuclides. Consequently

suitable synthetic procedures were devised. Following solvents were used for kinetic studies: 1-methylnaphthalene (MN), benzonitrile (BN) and propylene carbonate (PC). Labelled reagents 1 and 2 were separated by thin-layer chromatography and their radioactivites measured by liquid scintillation technique. In specially purified solvents no side reactions other than isomerization have been observed. For substrate concentrations of 1 - 10 mmol/l the reaction rate constants have been determined at temperatures 60-160°C with statistical errors ca. 2% at the 0,95 confidence level.

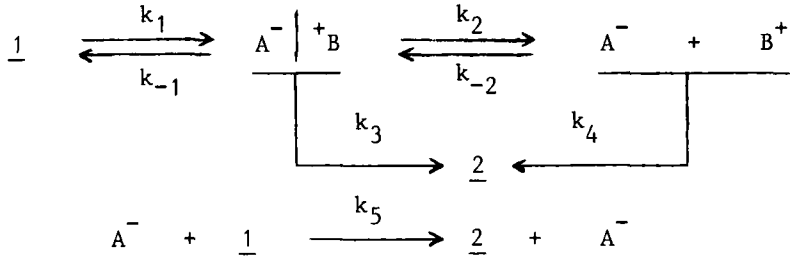
On the basis of the kinetic data two distinct isomerization reactions are shown.[2] First is the bimolecular reaction of thiopyrophosphate 1 with thiophosphate anion A^-:



This reaction proceeds as a typical $S_N2(P)$ displacement. The concentration of the anion A^-, which is regenerated as the leaving group, is constant. This type of the isomerization reaction is described by the first order kinetics: $^1k = {}^2k \cdot c_A$ and the anion acts as a catalyst. The energy of activation in MN solution of the reaction caused by thioacid AH is 74.2 kJ/mol. In BN solution the activation energy of the reaction caused by triethylammonium salt of this acid $AHNEt_3$ is equal to 72.9 ± 2.1 kJ/mol. This type of isomerization reaction is responsible for the lack of stability of symmetrical monothiopyrophosphates and their structural analogues.[1]

The second type of the isomerization is observed at higher temperature when high purity of substrate 1 and solvents is secured. In this case the reaction is also described by the first order kinetics. The observed activation energies of the reaction in MN and BN solutions are 128.2 ± 5.5 and 131.6 ± 2.9 kJ/mol, respectively. The apparent change in activation energies, close to 50 kJ/mol, supports

a concept of two different mechanisms. Our recent studies, presented below, are in favour of the dissociative mechanism operating in this case and described in the scheme:



In the first stage ion pairs $A^- \mid {}^+B$ are formed in equilibrium with ions A^- and B^+. These ionic species recombine to form the isomer 2. Formation of the anion A^- involves a contribution from $S_N2(P)$ pathway. Kinetic studies cannot define the structure of the cation B^+. It is reasonable to assume that this species is derived from the hypothetical parent cation $>\overset{+}{P}=O$ and solvent molecule. The complex of this type is not able to react with the substrate.

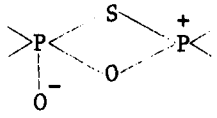
The formation of reactive ions in the second stage of reaction is only possible with particular solvent. These ions are not formed in MN solution. Their formation in BN and PC solutions is supported by the observed relationship between the rate constant k and the substrate concentration: $k = k_o + b\sqrt{c_1}$. The value of b is greater in PC as compared to BN solution. In turn, this value is close to zero in MN solution. The values of k_o are practically identical for all solvents applied.

This dissociative mechanism is supported by accelerating influence of lithium perchlorate added. Determined relationship between k and the concentration of $LiClO_4$ in BN suggests a specific salt effect.

The formation of reactive ions has been confirmed by a cross-checking experiment, in which the mixture of 1 with deuterium substituted isotopomer (methyl-$^2H_{12}$)1 has been used. Depending on the composition of the isotopomeric mixture in BN and PC solutions 10

- 20% of (methyl-$^{2}H_{6}$)2 was formed. The residue contained the isomer 2 and its (methyl-$^{2}H_{12}$)2 isotopomer.

The mechanism proposed in this paper is strongly supported by the studies[3-7] of the kinetic isotope effects. In these studies the substrate 1 was labelled with ^{36}S or ^{18}O at exocyclic positions. In theoretical calculations of the kinetic isotope effects of k_{16}/k_{18} and k_{32}/k_{36} two options of the mechanism have been considered. In the dissociative mechanism involving ion pair the primary kinetic isotope effect of sulfur is relatively high. On the contrary the oxygen secondary isotope effect is small. An alternative mechanism would involve a dipolar cyclic transition state or intermediate:



In this mechanism the values of isotope effects of sulfur and oxygen should be reverse. Experimentally determined[5-7] values of k_{16}/k_{18} and k_{32}/k_{36} are compatible with the ionic mechanism proposed.

The most interesting aspect of these studies is the evidence being in favour of a dissociative mechanism in the reaction which can be classified as ligand exchange at tetracoordinate phosphorus centre.

REFERENCES

1. J. Michalski, W. Reimschüssel and R. Kamiński, Usp. Khim., 47, 1528 (1978); Russ. Chem. Rev., 47, 814 (1978) and references therein.
2. R. Kamiński, Ph. D. Thesis, Lodz 1980.
3. R. Kamiński, P. Paneth and W. Reimschüssel, Spectrochim. Acta, 41A, 513 (1985).
4. W. Reimschüssel and P. Paneth, Org. Mass Spectrom., 15, 302 (1980).
5. W. Reimschüssel and P. Paneth, Anal. Chem., Symp. Ser., 11, 49 (1982).
6. P. Paneth, Ph. D. Thesis, Lodz 1984.
7. P. Paneth and W. Reimschüssel, J. Am. Chem. Soc., 107, 1407 (1985).