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W. Remschuessel<sup>a</sup>; J. Adamus<sup>a</sup>

<sup>a</sup> Institute of Applied Radiation Chemistry, Technical University, Zwirki, Lodz, Poland

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## SPONTANEOUS THIONO-THIOLO ISOMERIZATION OF THIONO-PHOSPHATES. DOES IT APPEAR WITHOUT IMPURITIES?

W. REMSCHÜSSEL and J. ADAMUS

Institute of Applied Radiation Chemistry, Technical  
University, Zwirki 36, 90-924 Lodz, Poland

Thiono-thiolo isomerization of O-alkyl esters of thiophosphoric acids to corresponding S-alkyl isomers has been extensively studied because of high biological activity of both esters. Such an isomerization proceeding without other reactants initially added is called thermal isomerization. Kinetic studies of this process allow to distinguish between reaction pathways of methyl esters  $A_2P(S)OMe$  leading only to S-methyl esters and of diesters  $AP(S)(OMe)_2$ , which give also other products. It is well known that the isomerization can be effected by organic bases (amines, phosphines), corresponding alkylonium thiophosphates, and protic acids. We decided to investigate the kinetics of thermal isomerization in solutions, to examine the influence of impurities of reactants or solvents for thiophosphates studied up to now appear to be not thoroughly purified. O,O-Diphenyl-O-methylthiophosphate, 5,5-dimethyl-2-methoxy-2-thio-1,3,2-dioxaphosphorinane and O,O-dimethyl-O-(4-nitro)phenylthiophosphate as model reactants and benzonitrile or 1-methylnaphtalene as solvents were chosen. We have found that the observed first-order rate constants  $k$  of the isomerization reaction significantly decreases (even 1000 times) with improving the purity of either the reactant or the solvent. The  $k$  values we could obtained may be considered to be the rate constant of either the thermal isomerization or the isomerization caused by residual impurities. For all the thionophosphate studied the activation energies of the thermal isomerization and the isomerization reaction with corresponding tetramethylammonium thiophosphates are practically the same. We believe that our findings may be of significant importance against the spontaneous isomerization of the thionophosphates studied.