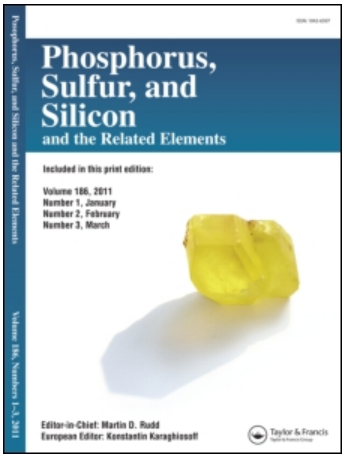

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Sulfur Isotopic Exchange Between Two Thiophosphoryl Compounds

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SULFUR ISOTOPIC EXCHANGE BETWEEN TWO THIOPHOSPHORYL COMPOUNDS

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Thiophosphoryl compounds are useful sulfur donors in thionation reactions (1,2) leading to P=S --> P=O exchange in thiation reagents. Although the reverse conversions P=O --> P=S are also known, mechanisms of both these types of reactions are not thoroughly studied. The analogy of chemical and isotopic exchange reactions in thiophosphoryl moiety push us to investigate the kinetics of isotopic exchange between two thiophosphoryl compounds.

In this communication we present kinetic data of sulfur isotopic exchange reactions between triarylphosphine sulfides and O,O-diaryldithiophosphates. Reactions occur in dilute solutions at temperature range 100-140 ^{o}C.

$$(RO)_2P(S)SH + R_3P\overset{*}{S} \rightleftharpoons (RO)_2P(\overset{*}{S})SH + R_3PS$$

Reactants were separated by TLC and their activities were determined by liquid scintillation technique. It was found that side-products formed during thermolysis of dithiophosphates are unreactive towards sulfur exchange. The rate constants determined for exchange with ^{35}S labelled phosphine sulfides or dithiophosphates are the same within the experimental error. The exchange reaction is first order with respect to both of reactants. The effect of reactants nature and solvent effects on rate constants and activation parameters have been determined. The proposed stepwise mechanism with two intermediates is supported by kinetic isotope effects k^H/k^D of dithiophosphates hydrogen.

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