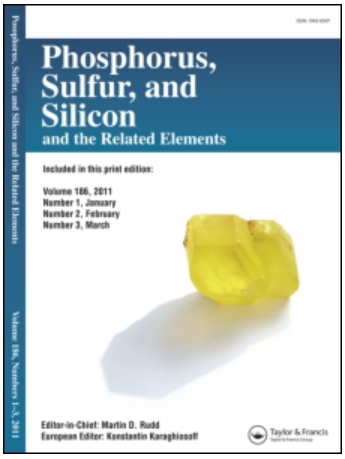

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Kinetics and Mechanism of Isotopic Exchange Reaction Between Elemental Sulfur and O,O-Diaryl Dithiophosphates

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KINETICS AND MECHANISM OF ISOTOPIC EXCHANGE REACTION BETWEEN ELEMENTAL SULFUR AND O,O-DIARYL DITHIOPHOSPHATES

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The salts derived from O,O-disubstituted dithiophosphates and tertiary amines are commonly known as useful starting materials in a variety of important organic syntheses including labelling with the ^{35}S (1, 2). The sulfur isotopic exchange reaction occurs in dry toluene at

$$(RO)_2PSSHNR'_3 + \overset{*}{S}_8 \rightleftharpoons (RO)_2P\overset{*}{S}SHNR'_3 + S_8 \qquad R = Ar;\ R' = Alk, Ar$$

temperature above 100°C. The reaction is exactly first order with respect to dithiophosphate, whereas the order in sulfur decreases from 1 to 0 with increase of sulfur concentration. Electron-withdrawing substituents in ester groups and electron-realesing substituents at nitrogen increase the reaction rate. The sulfur isotopic exchange does not occur practically in diaryl dithiophosphoric acids and their tetraethylammonium salts. The reaction mechanism, in which an isomerization of trialkylammonium dithiophosphate to an ion-pair $S\rangle P(S)\overset{+}{N}\langle|\bar{S}H$ precedes the exchange proper reaction with elemental sulfur, has been supported by kinetic isotope effect k^H/k^D of ammonium hydrogen. For the isotope exchange with either elemental sulfur or dibenzyl trisulfide the same values of both first-order rate constant and activation parameters of the dithiophosphate isomerization reaction have been determined.

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