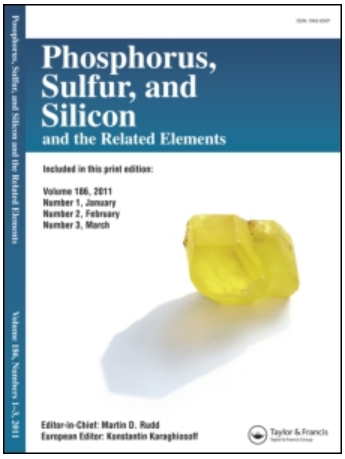

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KINETICS OF THE SUBSTITUTION REACTIONS OF ALKALI METAL PHENOXIDE WITH THE HEXAHALOCYCLOTRIPHOSPHAZENE RING: EXPERIMENTAL AND COMPUTATIONAL STUDIES

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The kinetics of the reaction of lithium, sodium, and potassium phenoxide with $P_3N_3X_6$ was studied (X = Cl, F). Solvent effects also were investigated from ion-solvating THF through diethyl ether to toluene. The reaction with lithium phenoxide was studied at several temperatures and the activation parameters evaluated. The data are consistent with an associative reaction mechanism involving a five-centered phosphorous intermediate. In contrast to earlier results in the literature studying reactions with amines, the rate-determining step in this case appears to be the addition of phenoxide to form the reactive intermediate, rather than the subsequent breaking of the phosphorous-halide bond. The higher positive charge of the fluorinated phosphorous centers produces an increase in rate over the chlorinated phosphorous centers. Computational results support the associative over the dissociative mechanism.

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