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Phosphorylation of Amine Compounds with Sodium Cyclo-triphosphate

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Among inorganic linear and cyclic phosphates, cyclo-triphosphate has drawn special attention for its high reactivity with various amine compounds. A ring opening reaction to produce N-alkylamidotriphosphate derivatives proceeds under moderate conditions, e.g., at room temperature in aqueous solution. In spite of its potentiality as a phosphorylating agent for amino groups, a systematic investigation on the reaction mechanism has not fully carried out. This may be due to the lack of analytical methods which allow the quantitative examination of the reactions. In this work, HPLC with an anion-exchanger column developed for phosphate compounds together with ³¹P-NMR were applied to a kinetic study. It has been clarified that; 1) the reactivity of amine compounds is primarily correlated with the basicity of the amino groups, i.e., pKa values of its conjugate acids, though, branching at α carbon of the amino group greatly retards the reaction rate because of steric hindrance, and 2) some bifunctional reagents, such as ethylenediamine, propanediamine, ethanolamine, and some α -amino acids produce heterocycles which contain P-N bond through an intramolecular reaction following the ring opening of cyclo-triphosphate. Ba or Mg salts of N-alkylamidotriphosphate derivatives have been prepared from mono amines, diamines, aminoalcohols, and aminoacids.