

Micellar Effects upon Phosphorylation and Phosphate Ester Hydrolysis

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The reactions between hydroxide or fluoride ion and p-nitrophenyl diphenyl phosphate, catalyzed by micelles of cetyltrimethylammonium bromide, are inhibited by phenyl, diphenyl, and p-t-butylphenyl phosphate. With decreasing pH the reaction with hydroxide ion becomes unimportant, and micellar-catalyzed reactions between the substrate and inorganic phosphate ions and phenyl and p-t-butylphenyl phosphate dianions can be observed. Diphenyl phosphate monoanion is unreactive. For the micellar catalyzed reaction the reactivity sequence is $t\text{-BuC}_6\text{H}_4\text{OPO}_3^{2-} > \text{C}_6\text{H}_5\text{OPO}_3^{2-} > \text{HOP}_4^{2-}$ and depends upon the nonbonding interactions between the cationic micelle and the nucleophilic anion, rather than their inherent nucleophilicities. The second-order rate constants for the micellar-catalyzed reaction with hydroxide ion agree well with those calculated at low pH in borate buffer. © 1969, American Chemical Society. All rights reserved.