

Micellar Effects on the Reactions of 2,4-Dinitrophenyl Phosphate and Ethyl p-Nitrophenyl Phosphate with Amines

Bunton, Clifford A.

Diaz, Simon

Hellyer, James M.

Ihara, Yasuji

Ionescu, Lavinel G.

The spontaneous hydrolysis of 2,4-dinitrophenyl phosphate dianion (I) is catalyzed by cationic micelles of the choline-derived surfactant (II, $n\text{-C}_{16}\text{H}_{33}\text{N}^+\text{Me}_2\text{CH}_2\text{CH}_2\text{OHBr}^-$), but this surfactant is no more effective than cetyltrimethylammonium bromide, CTABr. Zwitterionic micelles (III, $n\text{-C}_{12}\text{H}_{25}\text{N}^+\text{Me}_2\text{CH}_2\text{CO}_2^-$) are relatively ineffective catalysts. Added primary amines increase reaction rate in the presence of micelles of CTABr or II, but much of the rate enhancement is due to attack by amine upon the aryl group. The effect of the amine increases with its chain length, but secondary amines have less effect, and no attack on the aryl group was found with tertiary amines. The reaction of ethyl p-nitrophenyl phosphate monoanion in the presence of CTABr or II is slightly inhibited by added primary amine. In the absence of micelles, amines increase overall reaction rate by attacking the aryl group without markedly catalyzing hydrolysis. © 1975, American Chemical Society. All rights reserved.