

UNIVERSITY OF CALIFORNIA
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Micellar Effects upon the Hydrogen Ion and General Acid
Catalyzed Hydration of 1,4-Dihydropyridines

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ABSTRACT

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The rate limiting step in the hydration of 1-benzyl-1,4-dihydronicotinamide (1a) and 1-benzyl-3-acetyl-1,4-dihydropyridine (1b) is a slow proton transfer, as shown by the kinetic deuterium solvent isotope effects and buffer catalysis. Reactions in dilute HCl are strongly inhibited by cationic micelles of cetyltrimethylammonium bromide, CTABr, and the inhibition can be related to the micellar binding of the substrates determined spectrophotometrically or by solubility. Anionic micelles of sodium lauryl sulfate, NaLS, only weakly catalyze hydration in dilute HCl, and rate constants go through maxima with increasing [NaLS]. The dependence of rate on [NaLS] can be explained quantitatively in terms of substrate and hydrogen ion incorporation in the micelle and formation of an unreactive conjugate acid in the micelle. The equilibrium constants for unproductive protonation in the micelle corrected for reagent distribution are similar to those in water but the rate constants are lower. Micelles

of sodium n- dodecylhydrogen phosphate are good catalysts giving rate enhancements of ca. 10^3 relative to those in water.