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MICELLAR CATALYZED DECARBOXYLATION OF
6-NITROBENZISOXAZOLE-3-CARBOXYLATE ION

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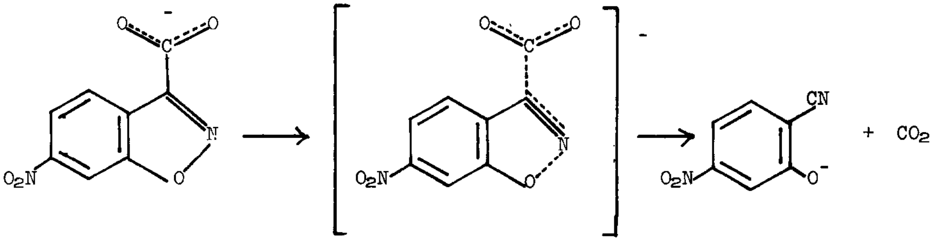
The rate of the spontaneous decarboxylation of benzisoxazole-3-carboxylate ions increases very markedly in going from water to less polar solvents and especially to dipolar aprotic solvents because of the differing solvation requirements of the initial state (I) with its localized charge and the transition state (II) with its more delocalized charge.[2] These solvent effects are very similar to those observed in the spontaneous solvolyses of 2,4- and 2,6-dinitrophenyl phosphate dianions.[3,4]



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We have found that cationic micelles of cetyltrimethyl ammonium bromide (CTABr) increase the rate approximately one hundred fold at the rate plateau when all the substrate is incorporated into the micellar pseudophase but that anionic micelles of sodium lauryl sulfate (NaLS) have little kinetic effect. The first order rate constants, k_ψ, are plotted against detergent concentration in Figure 1, for the decarboxylation of 6-nitrobenzisoxazole-3-carboxylate ion at 25.0° in aqueous solution (in the absence of detergent $10^6 k_\psi = 3.0\ \text{sec}^{-1}$). Changes in pH and buffer and substrate concentrations have little effect, provided that the pH is high enough for the substrate to exist predominantly as the carboxylate ion. Relatively high concentrations of a nonionic detergent, the polyether Igepal DM-730 (General Aniline and Film Corp.), increase the rate, probably due to the presence of micelles rather than a co-solvent effect because comparable concentrations (weight percentage) of bis (2-ethoxyethyl) ether increase the rate only slightly, and suggesting that the nonionic micelles can take up the carboxylate ion (I) at least partially. We found also that mixtures of CTABr and Igepal are better catalysts than either of the detergents alone suggesting that a co-micelle of cationic and nonionic detergent molecules is formed and that it is an excellent catalyst because of its lowered charge density. The rate is enhanced approximately 120 fold.

These micellar effects upon the rate of a reaction in which an existing charge is dispersed in the transition state are very similar to those observed for the spontaneous hydrolysis of anions of dinitrophenyl phosphates and sulfates,[5,6] and is consistent with the estimates of the properties at the surface of the micelle as compared to water.[7] At CTABr concentrations as high as 2.0×10^{-2} M, the observed rate constant remained the same as that observed in 3.8×10^{-3} M CTABr. The presence of a rate plateau rather than the rate maxima, typical of most micellar catalyzed reactions involving an external ionic reagent,[8,9] suggests that these maxima are not necessarily related to the increasing concentration of the counter ion of the detergent, but rather to deactivation of an external ionic reagent.

The substrate, as monohydrate m.p. 167-168° (lit. 167-168°), was prepared by conventional methods[10] and the reaction at 25.0° was followed spectrophotometrically at 410 mμ, using a Gilford spectrophotometer with a water jacketed cell compartment.

Kemp and Paul have suggested analogies between the environments of an aprotic solvent and that of a decarboxylating enzyme,[2] and analogies between micelles and enzymes have been widely discussed, and to some extent discounted,[8,9,11] but the present experiments support the principle that micelles catalyze reactions by changing the microscopic environment for reaction.

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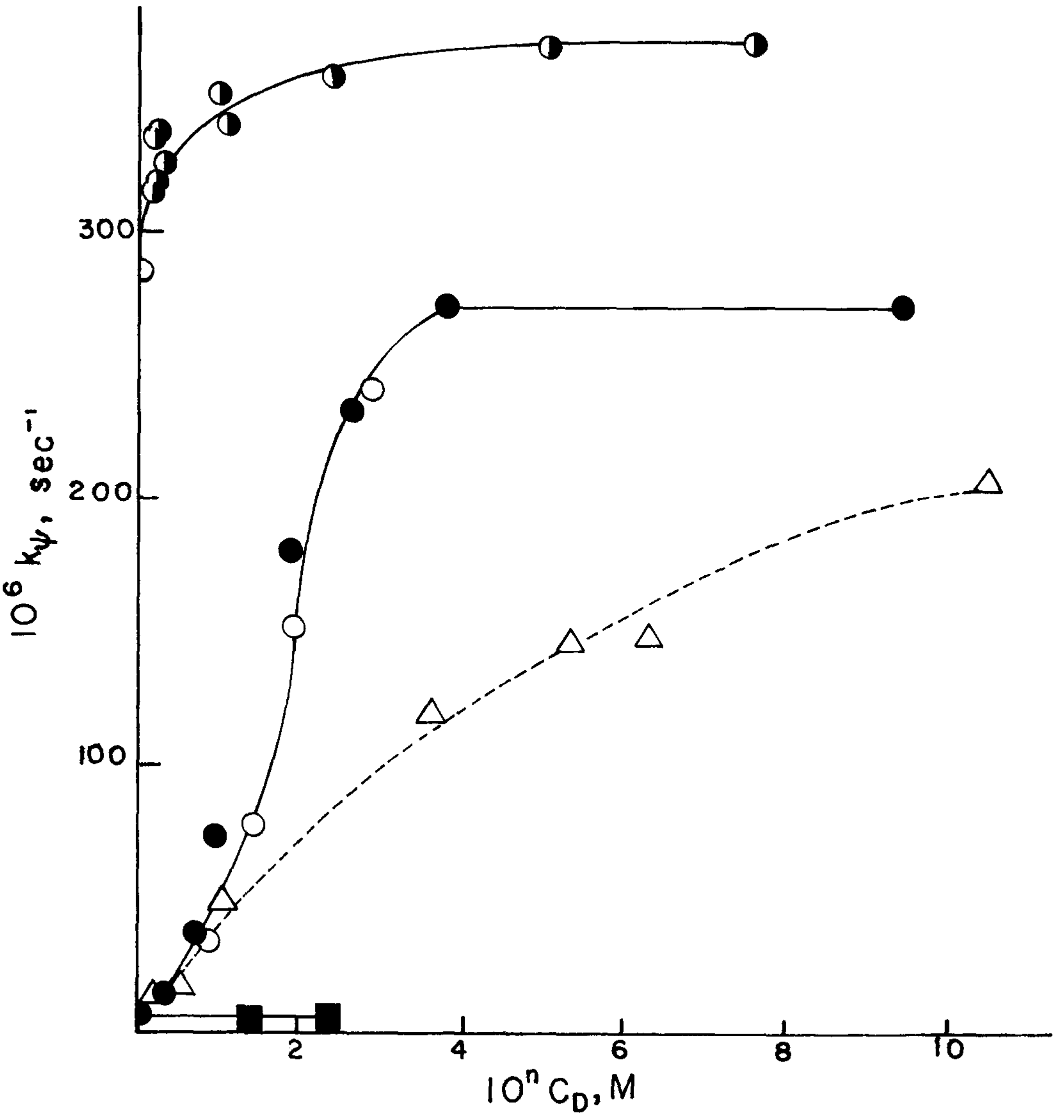

Figure 1. First order rate constants, k_ψ, of decarboxylation versus detergent concentration. ● 1.5×10^{-4} M substrate with 2×10^{-3} M NaOH in CTABr; ○ 5×10^{-5} M substrate with 2×10^{-3} M NH_4^+/NH_3 buffer at pH 9 in CTABr; ◐ 1.95×10^{-3} M CTABr + Igepal, pH 9; △ Igepal, pH 9; ■ NaLS, pH 9. For CTABr n = 3; for Igepal and NaLS n = 2.

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