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MICELLAR CATALYSIS OF THE BENZIDINE REARRANGEMENT

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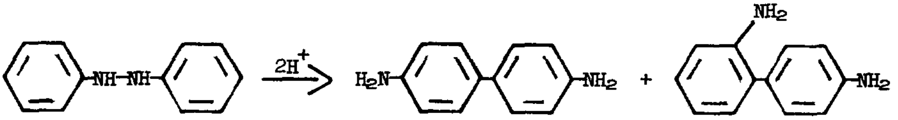
Anionic micelles accelerate specific hydrogen ion catalyzed reactions, but to date most information relates to hydrolyses.[1-3] We find a very large rate enhancement of the benzidine rearrangement of 1,2-diphenyl hydrazine (I) by anionic micelles of sodium lauryl sulfate (NaLS).[4] The rate enhancement, relative to reaction in dilute aqueous acid, is by a factor of 1.5×10^3, with a rate-surfactant profile typical of micellar catalysis, and a pronounced rate maximum (Fig. 1). In the absence of surfactant the values of $10^5 k_\psi$, the first order rate constant, are 1.5, 4.0 and 5.8 sec^{-1}, in 1.0, 1.65 and 2.0 mM HCl respectively. Cationic micelles of cetyl trimethylammonium bromide (CTABr) sharply inhibit reaction, by taking up the substrate into the micellar phase from which hydrogen ions are excluded, and nonionic micelles of Brij 58 slightly inhibit it. This inhibition by Brij may be a solvent effect, because addition of organic solvents often retards benzidine rearrangements. Slower reactions were followed using a Gilford spectrophotometer, and the faster reactions using a stopped flow spectrophotometer.



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The order with respect to hydrogen ions is approximately 2 in aqueous organic solvents,[5,6,7] and also in dilute HCl in the presence and absence of NaLS (Fig. 2). There is inevitably some uncertainty in the variation of k_m (the maximum value of k_ψ, Fig. 1) with acid concentration for the micellar catalyzed reaction, because of the distribution of hydrogen ions between the

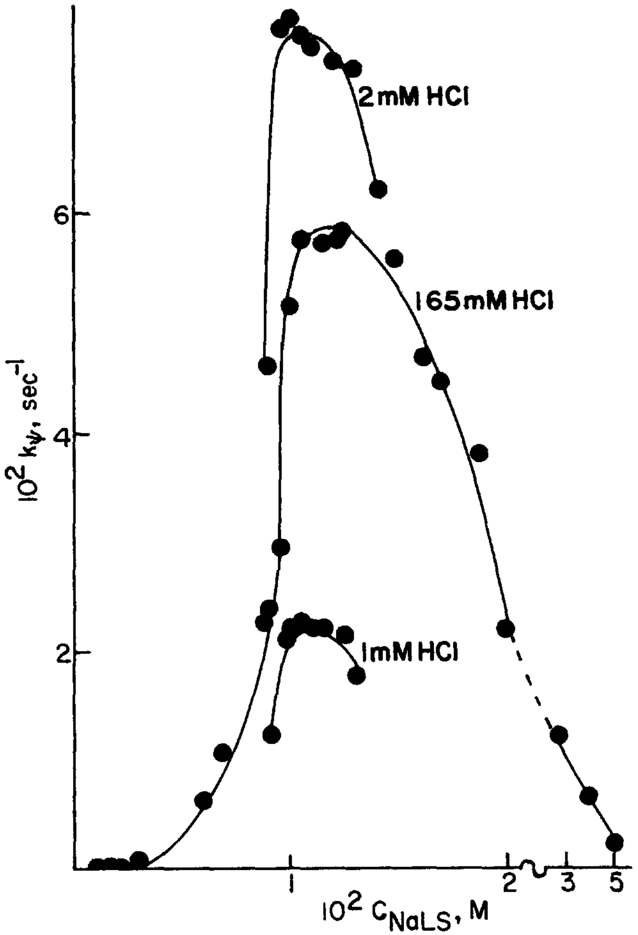

Figure 1. Effect of NaLS on the first order rate constant at 25.0°.

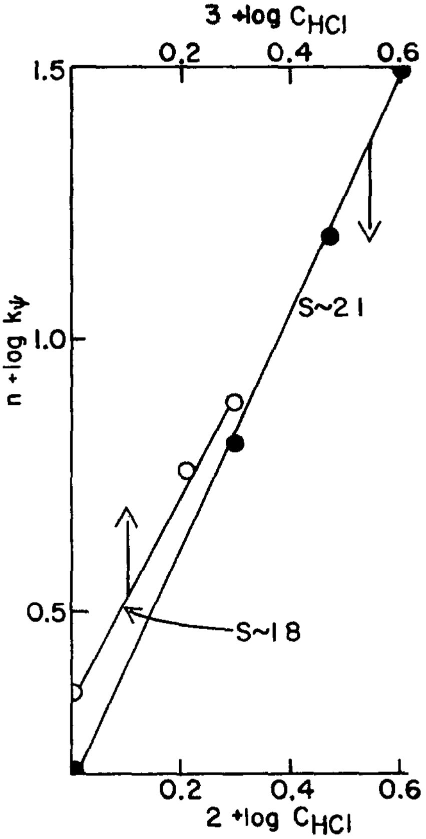

Figure 2. Dependence of rate on HCl, ● in water; ○ at optimum C_{NaLS}.

micelles and bulk solvent,[8] but it seems that the transition state involves two hydrogen ions for both micellar and non-micellar reactions.

The decrease of k_ψ at high C_{NaLS} can be explained in terms of the distribution of substrate and hydrogen ions between micelle and solvent, because once all the substrate is taken up into the micelles, addition of further surfactant reduces the probability of having substrate plus two hydrogen ions in the same micelle, *i.e.*, it dilutes the reagents in the micellar pseudophase.[8] This dilution effect is important only for reactions of greater than first order.

Anionic micelles do not change the product composition, which was 81% *p*-benzidine (II) in water and 79% in aqueous NaLS. The other product was diphenyline (III), determined spectrophotometrically,[6] and we were unable to detect any other products by paper or thin layer chromatography (c.f. ref. 5,6,9). In 95% EtOH the product is 70% p-benzidine and 30% diphenyline.[6]

This micellar rate enhancement, which is much larger than those generally found for specific hydrogen ion reactions, arises at least in part from the beneficial effects of the anionic micelles in bringing the three particles together in the micellar phase prior to formation of the transition state, and so increasing their effective concentrations and reducing the unfavorable entropy loss in forming the transition state (c.f. ref. 10 and 11).

The micellar catalysis of a one proton benzidine rearrangement should be less than of a two proton rearrangement, and this is observed for the rearrangement of 1,2-di-o-tolylhydrazine (IV). In aqueous organic solvents the rearrangement of (IV) shows a fractional order with respect to hydrogen ions,[5a] but in aqueous strong acid the reaction is first order with respect to hydrogen ions up to 0.01 M. In the absence of surfactant the first order rate constants in 1.65 and 2.1 mM HCl are 0.027 and 0.035 sec^{-1} respectively, but they are 1.53 and 2.37 sec^{-1} at the optimum concentration of NaLS, giving an approximately sixty fold micellar catalysis for this one proton rearrangement. In general, increasing reagent hydrophobicity increases micellar catalysis,[1-3] so that the smaller micellar rate enhancement of the rearrangement of (IV) relative to (I) must be related to the different molecularities of the reactions.

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