Catalysis by Reversed Micelles in Non-polar Solvents: Decomposition of 1,1-Dimethoxy-2,4,6-trinitrocyclohexadienylide Ion in Benzene

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Summary The rate constant for the decomposition of 1,1-dimethoxy-2,4,6-trinitrocyclohexadienylide ion in the presence of micellar dodecylammonium benzoate in benzene (containing 0·05% Me_2SO, v/v) is greater by factors of 62,900 and 1880 than those in benzene or in water; catalytic efficiency is markedly dependent on the Me_2SO concentration.

THE efficiency of enzymatic catalysis arises, at least in part, from favourable orientation of the substrate at the active site of enzymes.[1] The use of aqueous micellar systems as models has fallen short of initial expectations. Micelles rarely enhance the rates of reactions by factors greater than 100 and show only limited specificity.[2] It appears that aqueous micelles, unlike enzymes, are unable to hold substrates in a sufficiently rigid configuration with specific orientation. Solubilization of molecules in the polar environment of reversed micelles in non-polar solvents may provide a better approximation. Thus, we have reported recently that the mutarotation rate of 2,3,4,6-tetramethyl-α-D-glucose in benzene is enhanced by some 400-fold in the presence of reversed micelles and that this acceleration is considerably greater than that due to hydronium ions or water in aqueous solutions.[3] We have, therefore, examined the unimolecular decomposition of an ionic compound. Since the effects of aqueous micelles on Meisenheimer complex equilibria has been studied[4] and since nucleophilic aromatic substitution is of importance,[5] we now report dramatic rate enhancements for the decomposition of sodium 1,1-dimethoxy-2,4,6-trinitrocyclohexadienylide (**1**) in benzene by micellar dodecylammonium propionate (**2**), dodecylammonium butyrate (**3**), and dodecylammonium benzoate (**4**).

Preparation, purification, and characterization of (**1**),[4] (**2**),[6] (**3**),[6] and (**4**),[6] have been described. Reagent grade benzene was dried and stored over Linde Type 4A molecular sieve. Critical micelle concentrations of (**2**), (**3**), and (**4**) in pure benzene at 32° are $3{\cdot}0 \times 10^{-3}$M, $3{\cdot}8 \times 10^{-3}$M, and $4{\cdot}7 \times 10^{-3}$M, respectively. Solubilization of organic substrates, however, causes a substantial reduction in these values.[3] Decomposition of (**1**) was followed spectrophotometrically at 495 nm.[4] Runs were initiated by injecting 5·0 or 10·0 μl solutions of (**1**) in benzene–Me_2SO (75 : 25 v/v) to thermostated solutions of the surfactants in benzene. Rate constants, k_ψ, obtained from linear first-order plots (up to 95% reaction) are given in the Table. Me_2SO has significant effects on the catalytic efficiency of reversed micelles. At any given solvent composition increasing concentrations of the surfactants cause dramatic rate enhancements up to a maximum, followed by a short plateau and a subsequent decrease in the catalytic efficiency. In the plateau region in 0·05% Me_2SO–benzene (v/v) the rate constant for the decomposition of (**1**) in the presence of (**4**) is greater by a factor of 62,900 than that in pure benzene. Catalysis by (**2**) and (**3**) are of the same order of magnitude. It is perhaps more significant that the rate constant for the decomposition of (**1**) in benzene containing 0·05% Me_2SO in the presence of micellar (**4**) ($k_\psi = 943 \times 10^{-3}$ s^{-1}) is a factor of 1880 greater than that in water ($k_\psi = 5{\cdot}08 \times 10^{-4}$ s^{-1}).[4] The ionic complex (**1**) is likely to be oriented in the polar interior of the reversed micelle. Me_2SO as a co-solvent, even in very low concentrations, markedly stabilizes (**1**) with the resultant reduction in the micellar catalysis.

TABLE

Decomposition of 1,1-*dimethoxy*-2,4,6-*trinitrocyclohexadienylide ion*, (**1**) *in benzene containing* 0·05% *and* 0·10% Me_2SO (*v/v*) *in the presence of surfactants at* 24·5° [a]

	10^3k_ψ, s^{-1}	
10^4[Surfactant], M[b]	0·05% Me_2SO	0·10% Me_2SO
0·00[c]	0·0150	0·0145
0·10		0·016
0·20		0·022
0·50		19·8
0·75		62·9
1·00	195	75·9
2·50	713	193
2·50[d]	850	495
5·00	943	377
5·00[e]	345	168
7·50	888	407
10·0	851	449
25·0	638	327
50·0	568	285
75·0	451	308
100·0	391	241

[a] Concentration of (**1**) *ca.* 5×10^{-5}M; k_ψ values are the mean of 3 runs, each within ±6%. [b] Dodecylammonium benzoate (**4**) unless stated otherwise. [c] Decomposition of (**1**) in pure benzene. [d] Dodecylammonium butyrate. [e] Dodecylammonium propionate.

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