

CATALYSIS BY ZWITTERIONIC MICELLES IN AROMATIC NUCLEOPHILIC
SUBSTITUTION REACTION

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Abstract - The kinetics of the reaction of OH^- with 1-chloro-2,4-dinitronaphthalene (1) in the presence of *N,N*-dimethyl-*N*-tetradecylglycine (DTG) and *N,N*-dimethyl-*N*-hexadecylglycine (DHG) were studied. k_{obs} against [surfactant] increases sharply at low [surfactant] and then tends to level off either at low $[\text{OH}^-]$ added or at high $[\text{OH}^-]$ added. Rate effects were compared with those obtained in the presence of normal cationic micelles.

Introduction

Anionic and cationic micelles affect the rate of bimolecular reactions in water primarily because of the concentration of two reactants into a small volume.^{1,2}

Quantitatively these effects can be treated by assuming that micelles act as a pseudophase and bring reactants together, or keep them apart.

The interactions between micelles and ions (Coulombic and non-Coulombic interactions) markedly reduce the micellar charge in the Stern layer and for many ionic aggregates the fractional charge is very low.^{3,4,5}

It is generally accepted that the reactions in micellar pseudophase take place in the Stern layer.

It was reported⁶ that an additional charge on a ionic detergent in proximity of head group changes the catalytic efficiency.

It should be of general interest to study the effects of cationic micelle-forming agents which bear a negative charge in the proximity to the Stern layer.

We report here on our studies of the reaction of OH^- with 1-chloro-2,4-dinitronaphthalene (1) in the presence of betain-like surfactants and we compare their rate effects with those of cetyltrimethylammonium surfactants which form normal micelle in water.^{3,5}

Results and Discussion

Observed pseudo-first order rate constants for the aromatic nucleophilic substitution by OH^- (from NaOH or LiOH) on substrate (1) in the presence of *N,N*-dimethyl-*N*-tetradecylglycine (DTG) and *N,N*-dimethyl-*N*-

hexadecylglycine (DHG) are shown in Figures 1-3.

The rate-surfactant profiles in the presence of DTG show a catalysis for hydroxydehalogenation with a maximum effect at low concentration of surfactant and then, for each [NaOH] added, k_{obs} tends to level off with increasing [surfactant].

In the presence of DHG relatively low surfactant concentrations had to be used because of low solubility.

Rate enhancements by DTG and DHG, under the same experimental conditions, are very similar.

The rate-surfactant profile in CTACl micelles with [NaOH] 0.5 M is shown in Figure 4. The rate constant increases first to a maximum at low [CTACl] and then decreases gradually as the detergent concentration increases.

The rate-surfactant profiles for hydroxydehalogenation of (1) in the presence of colloidal aggregates formed from betain-like surfactant are similar to those observed for the reaction in cetyltrimethylammonium hydroxide (CTAOH) at high concentration of NaOH added (0.5 M),⁷ but different from those in the presence of cetyltrimethylammonium chloride and bromide (CTACl and CTABr) with the same amount of NaOH added. In fact in the presence of cationic micelles, CTAX (X= Cl, Br) and similar surfactants, k_{obs} reaches a maximum at relatively low [surfactant] and then k_{obs} decreases when the detergent concentration increases. This behaviour is general for $[OH^-]$ added until 0.5 M.

In the presence of CTAOH, in the absence or at low $[OH^-]$ added, k_{obs} increases when the surfactant concentration increases and at high $[OH^-]$ added the rate constant increases sharply near the C.M.C. of CTAOH and then reaches a plateau when the [surfactant] increases.⁷

The relatively hydrophobic substrate (1) is extensively micellar bound with $[CTAOH] \gg 10^{-2}$ M⁸ and when we add OH^- the effect on reactivity is related to an increase of bound OH^- . When the colloidal particles are saturated with OH^- an increase of $[OH^-]$ above 0.2 M should have little effect on k_{obs} .

We think that the rate-surfactant profiles for hydroxyhalogenation of (1) in betains can be explained in the same way.

The similar kinetic form at different [NaOH] added (Figure 1) agrees with the low C.M.C. of zwitterionic micelles.⁹ Thus the colloidal particles could be well defined at low surfactant concentration for each [NaOH] used and the hydroxydehalogenation of (1) sharply increases at low [betain] and goes to a plateau under conditions such that (1) should be essentially micellar bound and the micellar surface is saturated with OH^- .

The effects of [NaOH] are enough large to be ascribed to reactions in the aqueous pseudophase.

Fig. 1. Reaction of (1), in the presence of DTG, with NaOH: (■) 0.01 M, (▲) 0.05 M, (□) 0.1 M, (△) 0.3 M, (○) 0.5 M, at 25.0° C.

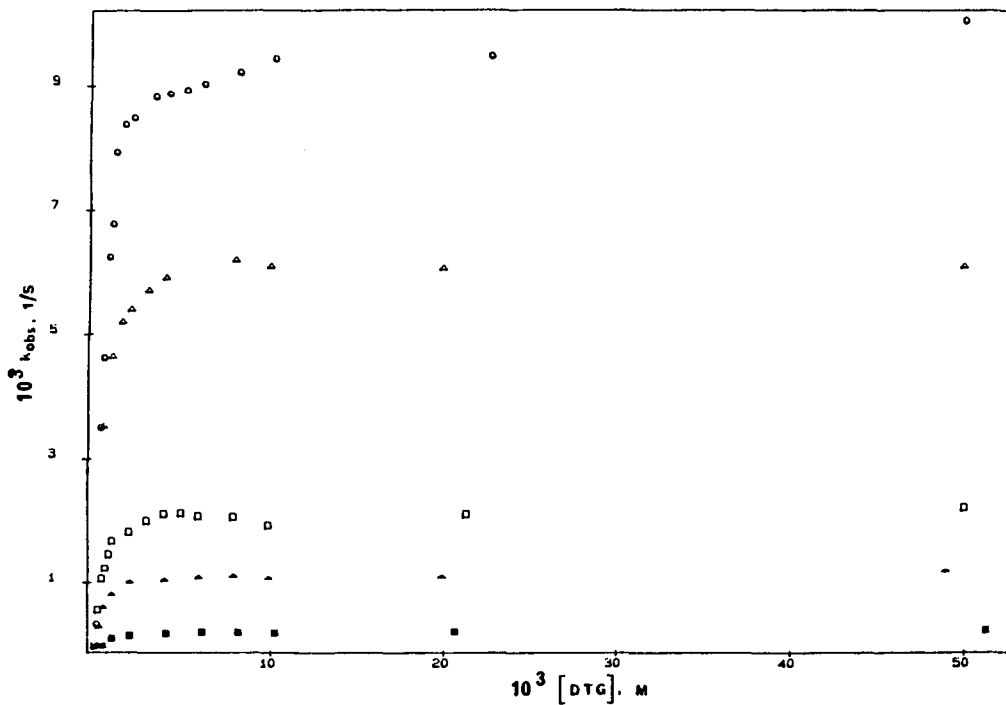


Fig. 2. Reaction of (1) with NaOH 0.5 M in the presence of DHG at 25.0° C.

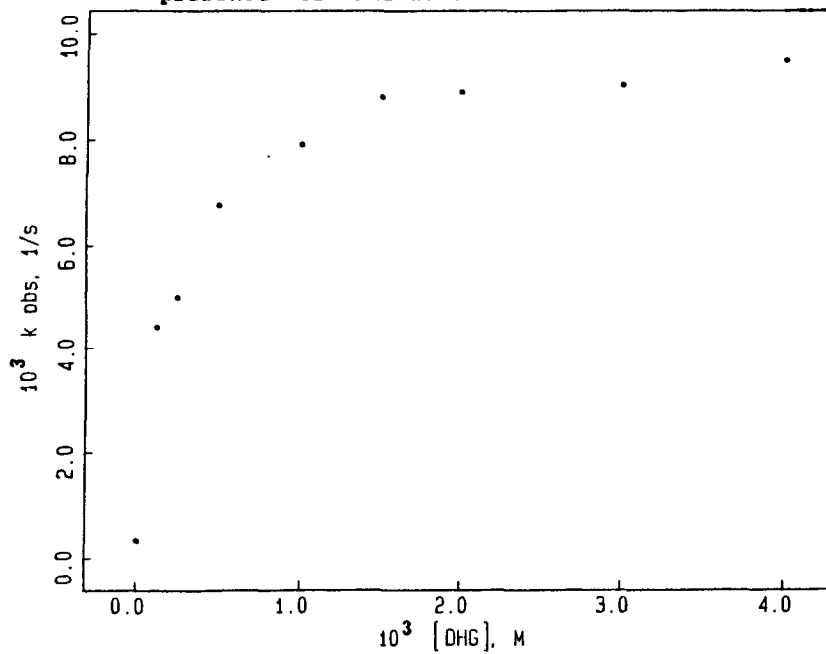


Fig. 3. Reaction of (1) with LiOH 0.5 M in the presence of DTG at 25.0° C.

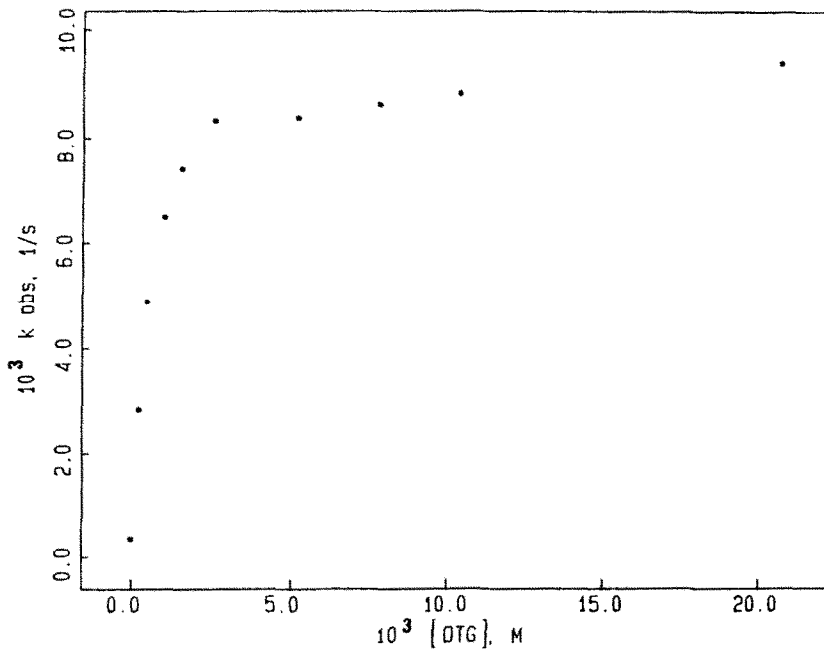
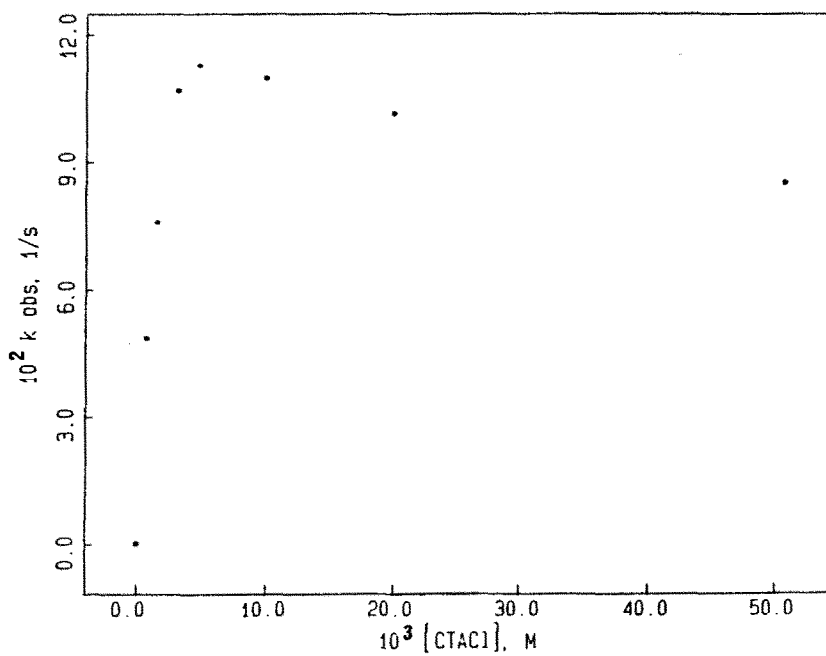


Fig. 4. Reaction of (1) with NaOH 0.5 M in the presence of CTACl at 25.0° C.



The rate enhancements are lower in the colloidal aggregates formed from betains than in CTAOH micelles or CTAX (X = Cl, Br) at the maximum.

Added salts inhibit reaction in dipolar micelles (Table 1) and the effects are smaller than in cationic micelles in fact in the last case the reactions with OH⁻ are almost completely suppressed by 0.2 M NaBr.⁵

The inhibitory effect of salt in the presence of betains like surfactants is consistent with general weak binding of ions to dipolar micelles. The inert anions interact with the quaternary ammonium centres in the micelle and reduce binding of OH⁻ so that the reactivity decreases.

From figures 1 and 3 we can see that the rate constants for hydroxydehalogenation of (1) in the presence of DTG with NaOH 0.5 M or with LiOH 0.5 M are almost the same and this probably because the interactions of cations are nonspecific and small. Hydration of the carboxylate ion will reduce their specific interactions with cations by hydrophobic or dispersive forces.

Table 1 - Salt Effects upon Reaction in the DTG Betaine.

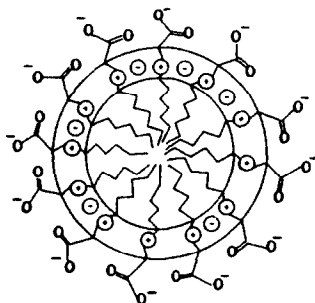
[NaCl], M	$10^3 k_{\text{obs}}, \text{ s}^{-1}$
0.01	5.8
0.05	5.3
0.10	4.5
0.20	3.8
0.30	3.4
0.40	3.2
0.50	3.0
0.84	2.0

Values in $8.1 \cdot 10^{-3}$ M DTG and 0.3 M NaOH. In the absence of added salt $10^3 k_{\text{obs}} = 6.2 \text{ s}^{-1}$.

These results suggest that the betain carboxylate head groups can attract anions from the aqueous region and the specific interactions are similar to those of cationic micellar head groups.

We can consider dipolar micelles formally as neutral colloidal particles and the interaction with free ions depend to a high degree upon the charge density at the micellar surface.^{3,10,11}

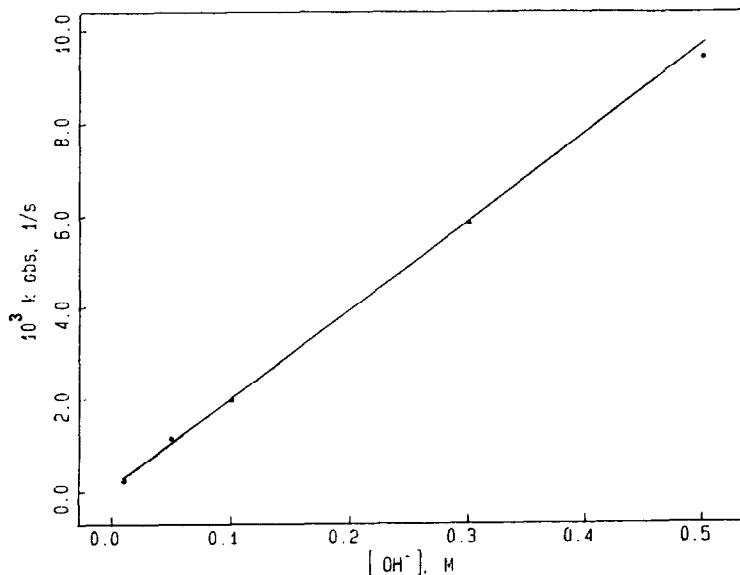
According to following model:



we can treat dipolar micelles as "smooth spheres" with the carboxylate ions extending from the quaternary ammonium centres and consequently the charge density at the spherical surface through these cationic centres will be greater than that at the spherical surface through the anionic centres, and there will be a net attraction of anions. This model is only a crude approximation, in fact we do not know the conformation of the dipolar head group in the colloidal particles, but it indicates how zwitterionic micelles could bind OH^- , although weakly, and why there is interionic competition.

The dependence of k_{obs} on $[\text{OH}^-]$ in the presence of DTG is showed in Figure 5. The linear increase of k_{obs} with $[\text{OH}^-]$ is consistent with the postulated weak binding of OH^- to dipolar micelles.

Fig. 5. Reaction of (1), in the presence of DTG 0.01 M, with NaOH at different concentrations and at 25.0° C.



It is known that in micellar solution where the counterion is extensively bounded, plots of k_{obs} against anion concentration curve down as counterions build up at the micellar surface.^{4,5}

Conclusions

The presence of a positive and negative charge in the same molecule of a surfactant plays an important role in the process of aggregation of these systems, and in the catalytic activity.

In fact the characteristic charge in zwitterionic microaggregates is not clear and there are three possibilities which must be reckoned.

First, dipolar micelles could influence the reaction rate of nucleophilic reactions like cationic micelles and accelerate the process.¹²

Second, zwitterionic colloidal systems may behave like anionic detergents which retard the reaction rate in alkaline hydrolysis since the positive charge of the cationic group should be neutralized by counterions at high ionic strength¹³ or because the particular interaction between the substrate and the micelle is in such a way that the reaction site should be deeply buried into the micellar pseudophase.¹⁴

Third, zwitterionic microaggregates could affect the reaction rate like neutral micelles and retard the nucleophilic reactions either on the basis of the ground state, or on the basis of the transition state as compared to the situation in cationic micelles.

On the basis of our results we can infer that zwitterionic micelles from DTG and DHG, qualitatively, behave like cationic micelles in accelerating the reaction rates of hydroxydehalogenation of (1).

The catalytic activity of the two zwitterionic surfactants, DTG and DHG, is smaller than that of classical cationic micelles substantially because of weak binding of OH^- to micellar surface.

Experimental

Materials.—Preparation and purification of surfactants and substrate have been described.^{9,14}

Kinetics.—Reactions were followed spectrophotometrically at 25.0°C using Beckman Model 35 or Perkin-Elmer 551S spectrophotometers. All solutions of surfactants were made up using CO_2 -free, redistilled water. Substrate solutions were made up in acetonitrile. Substrate concentrations were generally ca. $6 \cdot 10^{-5}$ M in cell holder. Reactions of (1) were followed at 390 nm.

Acknowledgements

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