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NUCLEOPHILICITY OF AZIDE ION IN THE MICELLAR PSEUDOPHASE.

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The reaction of azide ion with 2-chloro-3,5-dinitropyridine, n-butyl-4-nitrobenzenesulfonate and n-butyl-4-bromobenzenesulfonate is catalyzed by cationic micelles of cetyltrimethylammonium salt (CTAX, $X = Cl^-$, Br^-, $0.5\,SO_4^=$, OMes, N_3^-). The second-order rate constants in the micellar pseudophase is smaller than that in water.

The rates of many reactions are affected by micellized aqueous surfactant and it is generally accepted that incorporation of reactants into the micelles is of major importance. For example, cationic micelles catalyzed bimolecular reactions of nucleophilic or basic anions by incorporating both reactants into the small volume of the micellar pseudophase[1-6]. The variation of the observed first-order rate constant, k_ψ with concentrations of surfactant, counterions or added inert electrolyte can be explained in terms of a pseudophase model which treats the micelles as a reaction medium distinct from water[2,7,8]. It is possible to measure the distribution of the reactants between micelles and water directly or estimated provided that we assume that the two reactants bind independently, and second-order rate constants can be calculated in the micellar pseudophase[1-9]. Generally second-order rate constants in the micelle are not very different from those in water, so the micellar rates enhancements of bimolecular reactions are due largely to concentration of both reactants in the small volume of the micelles. Reaction of azide ion with 2,4-dinitrochlorobenzene and 2,4-dinitrochloronaphthalene is an exception to this generalization, because estimated second-order rate constants in the micelle are much larger than

Table 1. Reactions of 2a and 2b in $(CTA)_2SO_4$[a]

$10^3[(CTA)_2SO_4]$,M	2a	2b
0	4	1.7
1	142	36
2	169	52
4	179	54
7	175	49
10	151	43
30	94	23
60	61	15
100	44	12
150	26	8
180	22	7

[a] values of $10^5 k_\psi$ s^{-1} at 25.0°C with 0.01 M NaN_3.

those in water[10].

The discrepancy is apparently not due to abnormal binding of azide ion with bis(4-nitrophenyl)carbonate and methylbenzenesulfonate, second-order rate constants are very similar on micellar surfactants and in water[11,12].

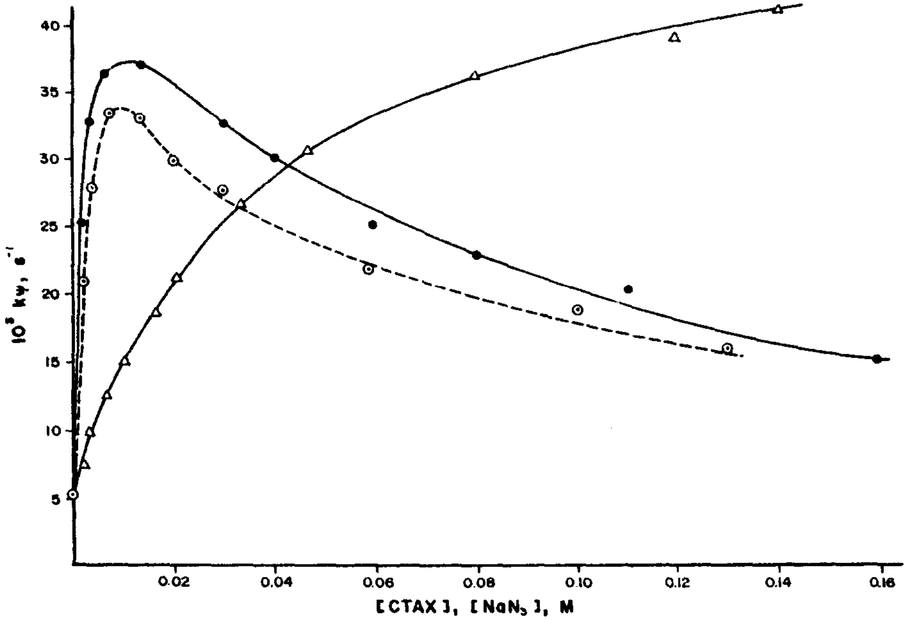


Figure 1: Reaction of 2-chloro-3,5-dinitropyridine with 0.01 M NaN$_3$
● in CTACl, ⊙ in CTABr, △ in 0.01 M CTABr and variable [NaN$_3$]

We were interested, therefore, in studying reactions of other substrates with azide ion in the presence of cationic surfactants.

Experimental

Materials: The preparation or purification of n-butyl-4-nitrobenzenesulfonate, n-butyl-4-bromobenzenesulfonate, CTABr, and CTACl followed standard methods[4,26]. The substrate 2-chloro-3,5-dinitropyridine from (Aldrich). CTAOMes was prepared in solution from CTAOH[14,23] by neutralization with equimolar methanesulfonic acid. The surfactant concentration was calculated from that of CTAOH. The preparation of $CTAN_3$ from $(CTA)_2SO_4$ and $Ba(N_3)_2$ in CO_2-free water and removal of $BaSO_4$ followed the method used for preparation of CTAOH[14,23,24].

Products. The substrate, 2-chloro-3,5-dinitropyridine was allowed to react with NaN_3 in aqueous MeCN and the azide products were identified by IR and

NMR spectrometry. The reactions of alkylbenzenesulfonate has been studied[10].

Kinetics. Reactions were followed spectrophotometrically at 25.0°C on Perkin Elmer by the decrease of absorbance at 456 nm for 2-chloro-3,5-dinitropyridine and 252 nm, 255 nm for n-butyl-4-nitrobenzenesulfonate and n-butyl-4-bromobenzenesulfonate respectively. For all reactions sbubstrate was added as a solution in MeCN to the reaction mixture in a 1 cm cuvette so that the concentration of the substrate was 10^{-5}M and the solution contain less than 1% MeCN. The first-order rate constant k_ψ , are in a reciprocal seconds.

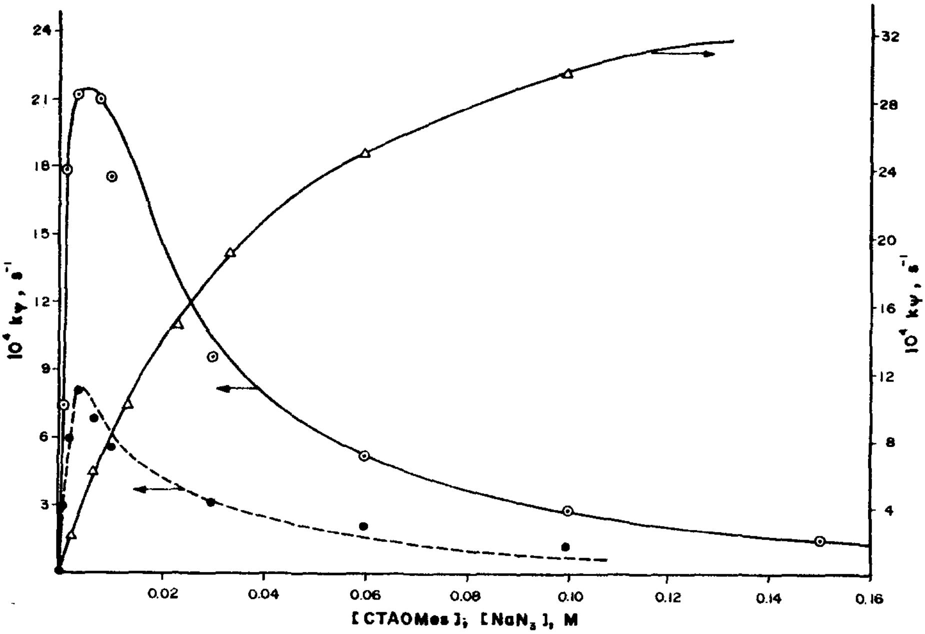


Figure 2: Reaction of n-butyl-4-nitro and 4-bromobenzenesulfonate with 0.01 M NaN_3 in CTAOMes

⊙ n-butyl-4-nitrobenzenesulfonate with 0.01 M NaN_3 in CTAOMes

● n-butyl-4-bromobenzenesulfonate with 0.01 M NaN_3 in CTAOMes

△ n-butyl-4-nitrobenzenesulfonate in 0.15 CTAOMes and variable [NaN_3]

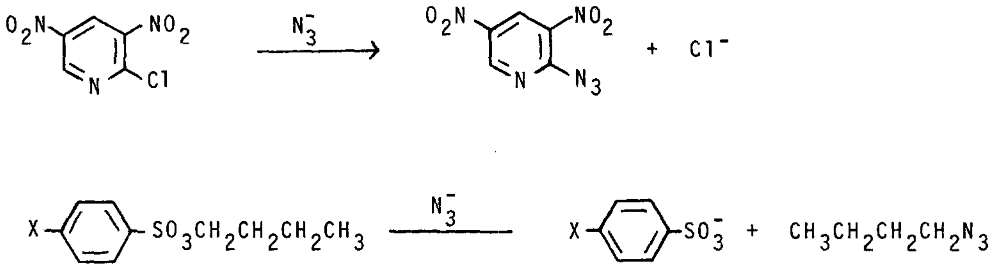
Results

Reactions in the Absence of Surfactant.

The second-order rate constant (k_W) for the reaction of 2-chloro-3,5-dinitropyridine is 0.5 $M^{-1}s^{-1}$. Reactions of N_3^- with substrate(1) occur by nucleophilic attack giving an azide products which is reasonably stable (Scheme 1). The second-order rate constants (k_W) for the reactions of n-butyl-4-nitrobenzenesulfonate (2a) and n-butyl-4-bromobenzenesulfonate (2b) are $4x10^{-3}M\ s^{-1}$

and $1.7\times10^{-3}M^{-1}s^{-1}$ respectively (Table II), scheme I.

Scheme I



2a X = NO_2 2b X = Br

Reactions in the Presence of Surfactants. Micellized cationic surfactants (CTAX, X = Cl, Br, OMes, 0.5 SO_4, N_3) speed reactions of substrate 1, 2a and 2b with N_3^- (Figures 1,2 and Table 1). As generally found k_ψ goes through maxima with increasing [CTAX] and constant $[N_3^-]$. Some reactions were followed in variable $[N_3^-]$ in constant [CTAX]. Under these conditions k_ψ increases steadly and reach a plateau (Figure 1 and 2). The rate-surfactant profiles are similar for reactions of all substrates.

Discussion

The kinetic analysis follow scheme II[13], where S is the substrate distributed between aqueous and micellar pseudophases denoted by the subscripts W and M respectively with reaction occuring in either pseudophase. The micellized surfactant (detergent) is denoted as D_n and its concentration is assumed to be given by [D]-cmc, where D is the surfactant cmc the critical micelle concentration which is assumed to be the concentration of monomeric surfactant, K_s is the binding constant of S to the micelles written in terms of micellized surfactant and k_W and k_M are first-order rate constants in aqueous and micellar pseudophases respectively.

Scheme II

$$\begin{tikzcd}
S_W + D_n \arrow[rr, shift left, harpoon] \arrow[dr, "k'_W"'] & & S_M \arrow[ll, shift left, harpoon] \arrow[dl, "k'_M"] \\
& \text{Products} &
\end{tikzcd}$$

So that the overall rate constant is given by eq 1[13].

$$k_\psi = \frac{k'_W + k'_M K_s [D_n]}{1 + K_s [D_n]} \qquad \ldots\ldots\ldots\ldots\ldots 1$$

Equation 1 is written in terms of the first-order rate constants for reactions in the aqueous and micellar pseudophases and they are given by eq 2 and 3[3,14,15], where k_W ($M^{-1} s^{-1}$) is the second-order rate constant for reaction in the aqueous pseudophase, $[N_3^-]$ is the molarity of the nucleophile (based

$$k'_W = k_W [N_3^-] \qquad \ldots\ldots\ldots\ldots\ldots 2$$

$$k'_M = k_M m_{N_3}^s \qquad \ldots\ldots\ldots\ldots\ldots 3$$

on total solution volume and neglecting the small volume of the micelles) and k_M (s^{-1}) is the second-order rate constant in the micellar pseudophase, corresponding to the concentration of N_3^-, written as a molar ratio, i.e eq 4[16,17]

$$m_{N_3}^s = [N_{3\,M}^-]/[D_n] \qquad \ldots\ldots\ldots\ldots\ldots 4$$

Equation 1-4 gives eq 5 and 6

$$k_\psi = \frac{k_W[N_{3W}^-] + k_M K_s m_{N_3}^s [D_n]}{1 + K_s[d_n]} \qquad \ldots\ldots\ldots\ldots\ldots 5$$

$$= \frac{k_W[N_{3W}^-] + K_M K_s [N_{3M}^-]}{1 + K_s[D_n]} \qquad \ldots\ldots\ldots\ldots\ldots 6$$

(The quantities in squared brackets are molarities in terms of the total solution volume).

For mixture of NaN_3 and CTAX we write the distribution of N_3^- between water and micelles in terms of eq 7[3,4,8,16-19]. The parameters in eq 6 and 7

$$K_X^{N_3} = [N_{3\,W}^-][X_M^-] / [N_{3\,M}^-][X_W^-] \qquad \ldots\ldots\ldots\ldots\ldots 7$$

can be estimated by fitting experimental rate-constant-surfactant profiles to these equations (Figure 1 and 2)[16,20].

Figure 1 illustrates the fit of the experimental and calculated date for some reactions of 2-chloro-3,5-dinitropyridine and the second-order rate constants, k_2^m are in Table II. The kinetically estimated values of K_s for 2-chloro-3,5-dinitropyridine are consistent with literature values of similar substrates such as 2,4-dinitrochlorobenzene[2,21,22].

Table II. Second-order Rate Constants in Aqueous and Micellar Pseudophases[a]

Substrates	Medium				
	H_2O	CTABr	CTACl	CTAOMes	$CTAN_3$
2-chloro-3,4-dinitropyridine[b]	0.5	5.5×10^{-3}	5.5×10^{-3}	-	4×10^{-3}
n-butyl-4-nitrobenzenesulfonate[c]	4×10^{-3}	-	-	3.4×10^{-4}	1.5×10^{-3}
n-butyl-4-bromobenzenesulfonate[c]	1.7×10^{-3}	-	-	1.3×10^{-4}	0.9×10^{-3}

[a]values of k_W and k_2^m M^{-1} s^{-1} in aqueous and micellar paseudophases respectively at 25.0°C, k_2^m is based on $K_{Br}^{N_3} = 2.5$, $K_{Cl}^{N_3} = 1.5$, $K_{OMes}^{N_3} = 1.1$ and $\beta = 0.7 - 0.8$, [b]$K_s = 70, 85$, in CTABr and CTACl respectively, [c] K_s = 115 and 130 for substrate 2a and 2b. in CTAOMes respectively.

Figure 2 illustrates the fit of experimental and calculated data for some reactions of n-butyl-4-nitrobenzenesulfonate and n-butyl-4-bromobenzenesulnate and the second-order rate constants, k_2^m are in Table II. Also the kinetically estimated values of K_s for both substrates are 115 and 125 m^{-1} respectively in CTABr and CTACl[20] and we use these values in treating our data in CTAMes and $CTAN_3$.

The reactions of substrate 1,2a and 2b where also followed in cetylmethylammonium azide ($CTAN_3$) in the absence of inert counterions and therefore with no ionic competition for the surface of the cationic micelles[20-24]. The observed first-order rate constants, k_ψ , under these conditions increases steadly to a plateau as substrate becomes fully micellar bound and the values of the second-order rate constants k_2^m calculated from these experiments are similar to those in mixture of CTAX and NaN_3 (Table II). The small differences between k_2^m in CTABr, CTAOMes and $CTAN_3$ are probably due to our assuming the same volume element of reaction for each surfactant.

The relation between k_W for reaction in water and k_M for reaction in the micellar pseudophase (eq 3) should provide information regarding the environmental effect of these two media on reactivity. The two sets of rate constants cannot be compared directly because of differences in their dimentions[15]. The second-order rate constant, k_M,is expressed in terms of concentration as a molar ratio of reactive anion to micellar head groups (eq 3) whereas for k_W the concentration is written, conventionally as a moles of nucleophile per liter of aqueous pseudophase which is approximated as total solution volume. The rate constants can be compared provided that the volume element of reaction pseudophase can be defined, which requires estimation of the molar volumes of the region of the micelle in which reaction occurs[2,4,8,15,19]. If one assumes that reactants are distributed uniformly over the micelle this volume element would be ca. 0.36[2,8,18], whereas if one assumes that reaction occurs only in the Stern layer, the volume element would be approximately half this values[3,15,16]. In other calculations we have used a volume of 0.14 L for reaction in CTABr and similar micelles, and we use this value here accepting that the selection is an arbitrary one. If different reactants are located preferentially in different regions of the micelle, it will be impossible to define a unique volume element of reaction.

On this basis the second-order rate constant k_2^m ($M^{-1}\ s^{-1}$) for reaction in micellar Stern layer is given by eq 8[14-16]. The second-order rate con-

$$k_2^m = 0.14\ k_M \qquad \ldots\ldots\ldots\ldots\ 8$$

stants for reactions of 2-chloro-3,5-dinitropyridine, n-butyl-4-nitrobenzenesulfonate and n-butyl-4-bromobenzenesulfonate with N_3^- are considerably smaller in micelles than in water (Table II).

These observation might be due to substrate (especially substituted alkylbenzenesulfonate) being located in the less aqueous region of the micelle. This explanation is supported by the observation that cationic micelles of cetyltrimethylammonium chloride or bromide inhibit hydrolysis of n-butyl-4-nitrobenzenesulfonate more than they do with methylbenzenesulfonate[4,26].

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