

bearing an extra proton: the k_a transition state has a negative ligand only partially attached, while the k_1 transition state has a fully attached negative ligand. As already noted, the half-filled circle for CH_2Cl in Figure 1b indicates weakly that a shift to a transition state resembling 4 (plus a proton) is occurring here; this was not taken into account in postulate II. The main effect of this error would be to change Figure 2f so as to increase the importance of w_1 compared to w_2 , while somewhat decreasing the importance of both compared to w_a . Nevertheless, the kinetic law would continue to depend chiefly on the k_a and k_2 processes.¹⁴

Postulate III has in effect already been defended in terms of structures 3 and 4 for the two k_2 transition states. The main requirement is that they should have, respectively, large and small ρ_I values, and this seems reasonable in terms of their structures, which place more and less negative charge, respectively, near R.

Experimental Section

Materials. Sodium hydroxide (Matheson, Coleman and Bell analytical reagents), potassium hydrogen phthalate (Fisher Chemical Co., dried at 110 °C before use), potassium chloride (Mallinkrodt Analytical Reagent; dried at 110 °C before use), and

(14) The deviation of the half-filled circle for CH_2Cl above the open circle corresponds to about 40-fold in the value of k_1 . In Table III, the ratio of k_2 to k_1 is 2640, so that their contributions are equal at $[\text{HO}^-] = 1/2640 = 3.8 \times 10^{-4}$ M. The corrected ratio is 66, so that the crossover point is now $[\text{HO}^-] = 1.5 \times 10^{-2}$ M. At the same time, the relative importance of k_a will be increased. Since the experimental measurements were all at $[\text{HO}^-] > 0.027$ M, the dominant terms will remain k_a and k_2 .

deuterium oxide (Bio-Rad Laboratories) were used without further purification.

Anilides. The mono-, di-, and trichloro-*N*-methylacetanilides were prepared by first allowing the corresponding acid to react with sulfuric chloride to form the acid chloride and then treating the latter with *N*-methylaniline in ethyl ether solvent. The precipitated product was recrystallized from an ethanol-water mixture. The melting points of mono-, di-, and trichloro-*N*-methylacetanilide were 67.5–69.0 °C (lit.¹⁵ mp 69 °C), 69.4–70.0 °C (lit.¹⁶ mp 69.9 °C), and 72.0–73.0 °C (lit.¹⁷ mp 72.5–73 °C), respectively.

Kinetics. The hydrolysis reactions were carried out under pseudo-first-order conditions (anilide concentrations typically about 10^{-4} M while the hydroxide ion concentrations varied from 10^{-2} – 10^{-1} M) at constant ionic strength (0.1 M in KCl). The reaction was followed by monitoring the production of *N*-methylaniline at 285 nm or at 235 nm, by use of a Beckman DU-2 spectrophotometer equipped with temperature-controlled cell compartments. The pseudo-first-order rate constants were evaluated by the Guggenheim method for each hydroxide ion concentration employed. The kinetic law best describing each set of data was identified by nonlinear least-squares regression analysis.

Registry No. 1 (R = CF_3), 345-81-3; 1 (R = CCl_3), 36558-96-0; 1 (R = CHCl_2), 23496-29-9; 1 (R = CH_2Cl), 2620-05-5; DOD, 7789-20-0; D_2 , 7782-39-0; HO^- , 14280-30-9.

Supplementary Material Available: Observed rate constants on which Table I is based (5 pages). Ordering information is given on any current masthead page.

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Micellar Effects on the Reaction of (Arylsulfonyl)alkyl Arenesulfonates with Hydroxide Ion. 1. Microenvironmental and Substituent Effects in the Stern Layer of Cationic Micelles¹

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The reaction of the sulfonates $p\text{-XC}_6\text{H}_4\text{SO}_2\text{CH(R)OSO}_2\text{C}_6\text{H}_4\text{Y-p}$ 1a–g with hydroxide ion (involving nucleophilic attack at sulfonate sulfur) is accelerated (7–25 times) in the presence of CTAB micelles (32.1 °C). The kinetic data are analyzed in detail by using the pseudophase ion-exchange (PPIE) model, taking into account partitioning of the reactants between the micellar and aqueous pseudophases and competition between hydroxide ions and detergent counterions for binding to the micelles. Binding constants obtained from the kinetic analysis are compared with those from ultrafiltration experiments. Generally, the PPIE model reproduces the experimental rate constants quite well, except at low detergent concentration (around the cmc). The second-order rate constants for reaction in the micellar pseudophase are 4–12 times smaller than those for reaction in bulk water. Therefore the observed catalysis is purely the result of the high local concentration of both reactants in the micellar pseudophase. The substituent effects for the reaction in the micelles reveal an increased susceptibility for variation of Y. No evidence for orientational effects was found. It is shown that the binding of the sulfonates with the micelles is mainly determined by the presence of the aryl groups. Based on a comparison with kinetic solvent effects on the reaction in 1,4-dioxane–water, it is suggested that the rates in the micellar pseudophase reflect a decrease in micropolarity at the binding sites of the substrate molecules.

Bimolecular micellar-catalyzed processes have been the subject of intensive research during the last 2 decades.² It is now firmly established that the bringing together or the separation of the reagents by the micelle are the

dominant factors in the micellar rate effects. Several kinetic treatments have been advanced to rationalize the micellar rate effects, including the enzyme,³ cooperativity,⁴ pseudophase,⁵ and the pseudophase ion-exchange (PPIE)⁶

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Table I. Catalysis and Inhibition by Micelles at 25 °C

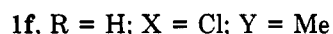
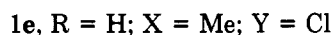
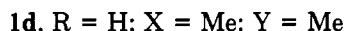
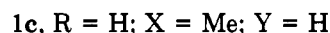
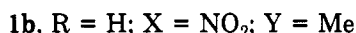
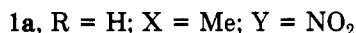
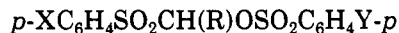
compd	detergent	cmc, ^a mM	[NaOH], mM	k_{exp}/k_w
1a	CTAB (3.4 mM)	0.92	5	25.0 ^b
1d	CTAB (2.2 mM)	0.92	5	9.7 ^b
1a	SDS (12 mM)	8.1	100	0.11
1d	SDS (12 mM)	8.1	500	0.04
1a	Igepal (1 mM)	0.16	100	0.50
1d	Igepal (1 mM)	0.16	500	0.50

^aAt 25 °C.² In the solutions containing 0.1 or 0.5 M NaOH the cmc's will be significantly lower. ^bMaximum rate increase induced by CTAB at [NaOH] = 5 mM and at 32.1 °C.

model. The PPIE analysis provides a particularly elegant way to describe quantitatively the catalysis or inhibition of *n*th order reactions involving a neutral substrate and hydrophilic reactant counterions in the presence of ionic micelles.

Despite these successful kinetic treatments, our understanding of microenvironmental and orientational effects on both reactants and the activated complex within the micelle is rather immature. It is usually assumed that solutes preferentially bind in the Stern layer of micelles at binding sites immersed in quite aqueous environments.^{2,7,8} But the nature of these binding sites may vary with subtle changes in the solute.⁹ Orientational effects in the solute-micelle binding process,¹⁰ which will directly affect the directionality of a chemical reaction in the Stern layer, are largely a matter of ignorance.

Herein we present a study of the reaction between the (arylsulfonyl)alkyl arenesulfonates 1a-g¹¹ and hydroxide



ions in the presence of cetyltrimethylammonium bromide (CTAB) micelles. Particular attention is focused on the substituent effects on the reaction rates in the presence of the micelles in terms of the Hammett free energy relationship. The kinetic data are primarily analyzed according to the PPIE model.⁶

Results and Discussion

Previous studies from our laboratory¹² have shown that the reaction of 1a-g with hydroxide ions proceeds via

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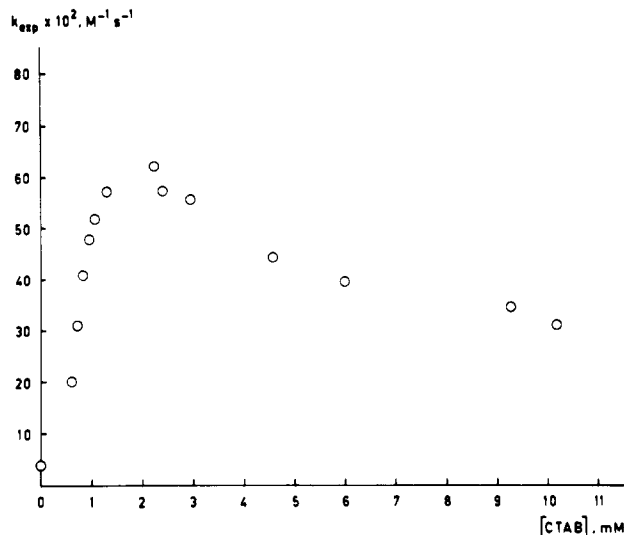
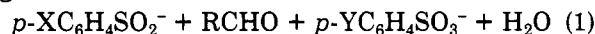
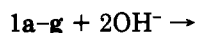


Figure 1. Second-order rate constants for the reaction of 1e in the presence of 5 mM NaOH and CTAB micelles at 32.1 °C.

nucleophilic attack of OH⁻ at the sulfonate sulfur atom (eq 1). The Hammett ρ values ($\rho_x = 0.49$, $\rho_y = 2.12$)¹¹ are



indicative for a considerable amount of charge transfer from the nucleophile to the electrophilic sulfonate reaction site. However, it is not completely clear at the moment whether the reaction involves a synchronous S_N2-type mechanism or an addition-elimination route via a penta-coordinated sulfur intermediate.¹²

Micellar effects on the reaction of 1a-g with OH⁻ follow the simple Hartley rules: the rates are enhanced in the presence of cationic micelles (CTAB) but retarded by anionic (SDS) or nonionic (Igepal) micelles (Table I). All sulfonates experience a maximum rate increase (k_{exp}/k_w ; k_w is the rate constant in the absence of micelles) of 7–25 times in the presence of micellized CTAB at 32.1 °C (Table IX, supplementary material); a characteristic plot of k_{exp} vs. [CTAB] for 1e is shown in Figure 1. Starting from the cmc there occurs a rather abrupt increase in k_{exp} , reflecting a highly efficient uptake of the substrate by the CTAB micelles. Then the rate goes through a maximum and decreases at still higher concentrations of CTAB. This behavior is normal for micellar-catalyzed bimolecular processes.^{2,5} In order to account for the kinetic complexity introduced by the fact that the binding of the reactant ion (OH⁻) to the micelles is determined by a competition in binding between OH⁻ and the detergent counterion (Br⁻), the data will be analyzed in terms of the PPIE framework.⁶ We note, however, that there is controversy whether or not the total degree of ionization (α) of the micelle is constant under conditions of varying counterion concentrations.^{6,13–15} Several attempts have been made to circumvent some of these problems,^{13,16,17} but they usually did not lead to an efficient simplification of the kinetic analysis.

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Table II. Analysis of the CTAB-Catalyzed Reaction of 1e with Hydroxide Ions according to the PPIE Model^a

[CTAB], mM	[NaOH], mM	cmc, ^c mM	$k_{\text{exp}} k_w^{-1}$	D , ^d mM ²	D' , ^e mM ²	$[\text{OH}]_{\text{m,calc}}$, ^f mM	$k_M(k_w \bar{V})^{-1}$, ^d mM	$k'_M(k_w \bar{V})^{-1}$, ^e mM
3.00	5.0	0.60	15.0	199	215	0.214	928	1002
4.00	5.0	0.60	13.5	245	261	0.255	959	1022
6.00	5.0	0.60	10.4	291	304	0.310	938	979
8.00	5.0	0.60	9.0	342	353	0.346	987	1019
1.50 ^b	5.0	0.16	3.78	29	32	0.030	969	1088
3.00 ^b	5.0	0.18	4.73	71	76	0.073	968	1031
4.50 ^b	5.0	0.23	5.81	130	136	0.134	965	1010
6.00 ^b	5.0	0.32	6.89	203	210	0.222	911	944
7.50 ^b	5.0	0.60	9.14	324	336	0.338	957	994
7.48	5.0	0.60	8.78	313	322	0.338	926	951
7.48	24.0	0.36	5.95	1026	1077	1.158	886	930
7.48	41.0	0.30	4.76	1402	1479	1.607	872	920
7.48	60.2	0.26	4.19	1822	1918	1.979	920	969
7.48	79.5	0.24	3.73	2148	2257	2.266	948	996
7.48	99.0	0.22	3.51	2524	2647	2.503	1008	1057

^a 32.1 °C; $k_w = 3.71 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$. ^b Measurements at a constant bromide ion concentration: $[\text{CTAB}] + [\text{NaBr}] = 7.5 \text{ mM}$. ^c cmc's were obtained from conductivity measurements. ^d D was calculated from the kinetic data, according to eq 3. The fraction f_S of micelle-bound 1e was calculated from the ultrafiltration binding constant¹⁸ K_S and ranges between 0.84 and 0.99. $k_M(k_w \bar{V})^{-1}$ equals the ratio $D/[\text{OH}]_{\text{m}}^{-1}$ [eq 3]. ^e D' and $k'_M(k_w \bar{V})^{-1}$ were calculated as described in note d. A somewhat lower "kinetic" binding constant ($K' = 2 \text{ mM}^{-1}$, see text) was used. The f'_S values range between 0.73 and 0.94. ^f $[\text{OH}]_{\text{m}}$ was calculated from eq 5 with $K_{\text{OH/Br}} = 0.04$ and $\alpha = 0.25$.

For practical reasons, the CTAB-catalyzed reaction of 1e was chosen for a detailed analysis. Three series of rate measurements are compared (Table II). Firstly, the detergent concentration was changed at constant hydroxide ion concentration. Secondly, the same experiments were performed at a constant bromide ion concentration. Finally, the hydroxide ion concentration was changed at a constant detergent concentration. In the latter case, an approximately inverse dependence of the second-order rate constant on the hydroxide ion concentration was found. For this series only those rate constants were used for which it can be safely assumed that more than 80% of the sulfonate molecules are bound to the micelles.¹⁸ Consequently, the data in Table II reflect the relative binding of hydroxide and bromide ions as well as the dilution of hydroxide ions and sulfonate in the micellar phase at higher detergent concentrations. We start from eq 2,⁶ in

$$k_{\text{exp}} k_w^{-1} = f_S f_{\text{OH}} k_M k_w^{-1} (C \bar{V})^{-1} + (1 - f_S)(1 - f_{\text{OH}}) \quad (2)$$

which f_S and f_{OH} are the fractions of sulfonate and OH^- , respectively, sorbed by the micelles, k_M and k_w are the second-order rate constants for reaction in the micellar and aqueous pseudophase, respectively, and $C \bar{V}$ represents the volume fraction of the reaction medium occupied by the micellar pseudophase.^{5,6} Assuming that $(1 - f_{\text{OH}})$ equals one, which is realistic under the employed reaction conditions, eq 2 can be written as eq 3, in which C is the

$$D \equiv [\text{OH}]_{\text{t}} C [(k_{\text{exp}} k_w^{-1} - 1) f_S^{-1} + 1] = k_M [\text{OH}]_{\text{m}} (k_w \bar{V})^{-1} \quad (3)$$

concentration of micellized detergent, \bar{V} is the partial molar volume of the micellized detergent molecules, and $[\text{OH}]_{\text{t}}$ and $[\text{OH}]_{\text{m}}$ are the total concentration of OH^- ions and the concentration of OH^- ions (with respect to the total solution volume) bound to the CTAB micelles. The term D is calculated (Table II) by means of substrate binding constants obtained from both kinetic and ultrafiltration experiments.^{1,18} In order to obtain the true micellar rate effect $k_M(k_w \bar{V})^{-1}$, the concentration $[\text{OH}]_{\text{m}}$ must be known. The fraction of bound OH^- ions is determined by the degree of ionization (α) of the micelle and by the ion-exchange constant⁶ $K_{\text{OH/Br}}$. Thus, a constant value should be found upon dividing D by $[\text{OH}]_{\text{m}}$. An iterative proce-

Table III. Calculated and Observed^{a,b} Second-Order Rate Constants for the Reaction of 1e with Hydroxide Ions in the Lower Micellar Concentration Region

[CTAB], mM	$[\text{OH}]_{\text{m,calc}}$, ^c mM	$f_{S,\text{calc}}$, ^d	$f'_{S,\text{calc}}$, ^d	$10^2 k_{\text{calc}}$, ^e M ⁻¹ s ⁻¹	$10^2 k'_{\text{calc}}$, ^e M ⁻¹ s ⁻¹	$10^2 k_{\text{exp}}$, ^e M ⁻¹ s ⁻¹
0.80	0.033	0.444	0.286	54.5	38.4	39.0
1.00	0.062	0.615	0.444	68.1	53.0	50.1
1.20	0.085	0.706	0.545	71.4	59.5	57.5
1.50	0.116	0.783	0.643	71.3	62.8	63.1
2.00	0.156	0.848	0.737	66.8	62.0	63.1

^a At 32.1 °C, $[\text{NaOH}] = 5 \text{ mM}$, $\text{cmc} = 0.6 \text{ mM}$. ^b k_{calc} has been calculated from eq 2, using f_S values and $k_M(k_w \bar{V})^{-1} = 942 \text{ mM}$. The k'_{calc} values were obtained from f'_S and $k'_M(k_w \bar{V})^{-1} = 1000 \text{ mM}$. ^c Obtained from eq 5. ^d Calculated fractions of micellar-bound 1e from $f_S = KC(KC + 1)^{-1}$ and using binding constants of 4 and 2 mM⁻¹, respectively.

cedure was adopted by varying independently $K_{\text{OH/Br}}$ and α in order to calculate the best $k_M(k_w \bar{V})^{-1}$ value. We find $k_M(k_w \bar{V})^{-1} = 942 \text{ mM}$ (standard deviation $\pm 4\%$) using $K_{\text{OH/Br}} = 0.0400 \pm 0.0024$ and $\alpha = 0.25 \pm 0.02$.¹⁹ Using eq 4,²⁰ we calculate that maximally 10% of the total hydroxide ions can be bound by micellar CTAB.

$$(f_{\text{OH}})_{C \rightarrow \infty} = K_{\text{OH/Br}} [K_{\text{OH/Br}} + \alpha(1 - \alpha)^{-1}]^{-1} \quad (4)$$

With $k_M(k_w \bar{V})^{-1} = 942 \text{ mM}$, $K_{\text{OH/Br}} = 0.04$, and $\alpha = 0.25$, the catalysis in the lower micellar concentration range can be calculated by means of eq 2 and 5:^{6,20}

$$f_{\text{OH}} = [\text{OH}]_{\text{m}} [\text{OH}]_{\text{t}}^{-1} = -B(2A)^{-1} + \{B^2(2A)^{-2} - EA^{-1}\}^{1/2} \quad (5)$$

in which

$$A = (1 - K_{\text{OH/Br}}) \quad B = -E + K_{\text{OH/Br}} + \{\text{cmc} + [\text{NaBr}]\} [\text{OH}]_{\text{t}}^{-1} + \alpha C [\text{OH}]_{\text{t}}^{-1}$$

and

$$E = -(1 - \alpha) K_{\text{OH/Br}} C [\text{OH}]_{\text{t}}^{-1}$$

(19) Previous values^{13,15,20} for $K_{\text{OH/Br}}$ are in the range 0.03–0.08 and for α in the range 0.20–0.29. For a discussion of factors that affect the binding of anions to CTA micelles, see: Gamboa, C.; Sepúlveda, L.; Soto, R. *J. Phys. Chem.* 1981, 85, 1429.

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(18) Based on ultrafiltration experiments: van de Langkruis, G. B.; Engberts, J. B. F. N. *Tetrahedron Lett.* 1979, 3991.

Table IV. Binding Constants and Relative Micellar Rate Constants Calculated on the Basis of the PPIE Model^a

compd	$k'_M(k_w\bar{V})^{-1}$, mM	K' , mM ⁻¹	K_S , ^b mM ⁻¹	$k_M(k_w\bar{V})^{-1}$, ^b mM
1a	2000	0.8	3.0	1700
1b	800	0.8	(3.0)	650
1c	600	0.9	(3.1)	525
1d	670	1.1	(3.3)	600
1e	1000	2.0	4.0	942
1f	875	0.9	(3.1)	

^a Using eq 2 and 5. The accuracy of K' is about $\pm 10\%$. The cmc is ca. 0.6 mM. ^b The best $k'_M(k_w\bar{V})^{-1}$ values were derived from rate constants at higher (>3 mM) CTAB concentrations (see text) adopting the K_S values.

The results are summarized in Table III. In this analysis the validity of the PPIE model can be checked with respect to the binding of 1e. Particularly at the lower micellar concentrations (<2 mM) we find that k_{calc} is significantly larger than k_{exp} . A better consistency is obtained with a smaller "kinetic" binding constant K' (2 mM⁻¹) and a somewhat larger micellar catalytic activity $k'_M(k_w\bar{V})^{-1}$ (1000 mM).

The same parameters $K_{\text{OH/Br}}$ and α were employed in the analysis of the kinetic data of the remaining sulfonates. The results are given in Table IV and comprise the best values for $k'_M(k_w\bar{V})^{-1}$ and K' . Binding constants obtained by ultrafiltration experiments (1a, 1e) are denoted by K_S . The values for 1b–d were estimated from linear interpolation of those for 1a and 1e, taking K' values as a reference.

The differences between the K' values and the K_S values are too large to be insignificant. Apparently, the low values of K' are caused either by a too low catalytic activity in the low concentration region or by a too high catalytic activity in the high detergent concentration zone. One could assume that the cmc is changed by the 10^{-5} – 10^{-4} M concentrations of the sulfonates, but this phenomenon will exert only a minor effect on the reaction profile.²¹ This is also the case for a possible effect of a decrease in monomer detergent concentration at higher detergent concentrations.²² A possible explanation involves an interaction between several sulfonate (or product) molecules with small, immature micelles in the concentration range just below the cmc, thereby inducing the formation of small clusters of relatively low dynamic basicity of bound OH⁻ ions. The observation of catalytic activity below the cmc is consistent with this idea. The ultrafiltration experiments¹⁸ definitely show that no large micellar aggregates are present below the cmc. We note that similar micellar activities inconsistent with the PPIE model have been described previously.²³

Our evaluation of the predictive power of the PPIE model is summarized in Table V, employing both the low and higher binding constants. The most serious deviation from the PPIE model occurs for 1a at low CTAB concentration. At these detergent concentrations (<1.5 mM) the "weak-binding" rate constants k_{calc}/k_w^{-1} provide the best agreement with experiment. At more elevated detergent concentrations the reverse is often true. Interestingly, this partial failure of the PPIE model tends to disappear at higher OH⁻ concentrations, as exemplified by the $k_{\text{calc}}k_w^{-1}$

Table V. Comparison of Observed and Predicted Micellar Catalytic Effects^a Using the PPIE Model

compd	[CTAB], mM	[NaOH], mM	cmc, ^b mM	$k_{\text{exp}}k_w^{-1}$	$k'_{\text{calc}}k_w^{-1}$ ^c	$k_{\text{calc}}k_w^{-1}$ ^c
1a	3.13	2.41	0.75	34.6	24.7	27.8
1a	0.693	10.0	0.49	10.4	9.2	19.8
1a	0.811	10.0	0.49	13.0	12.3	24.0
1a	0.941	10.0	0.49	16.0	14.8	26.3
1a	1.25	10.0	0.49	18.6	18.4	28.1
1a	0.848	7.5	0.54	12.9	12.7	25.2
1a	1.02	7.5	0.54	18.6	16.3	28.5
1a	1.37	7.5	0.54	22.2	20.2	30.1
1a	1.61	105.2	0.22	7.60	6.1	7.6
1e	1.424	2.01	0.78	22.9	16.1	19.2
1e	1.424	3.16	0.70	21.0	16.7	19.5
1e	1.64 ^d	5.00	0.02	0.54	0.38	0.28
1b	3.05	50.0	0.28	4.70	4.40	4.41
1b	1.35	50.0	0.28	4.65	4.13	5.06
1c	0.300	100	0.22	1.44	1.21	1.53
1c	0.416	100	0.22	1.78	1.46	1.97
1c	0.572	100	0.22	2.08	1.71	2.29
1c	0.810	100	0.22	2.37	1.97	2.50
1c	1.51	100	0.22	2.63	2.29	2.50
1c	3.02	100	0.22	2.63	2.33	2.35
1c	8.49	100	0.22	1.89	1.85	1.69
1d	0.300	100	0.22	1.71	1.30	1.67
1d	0.416	100	0.22	2.20	1.63	2.21
1d	0.572	100	0.22	2.60	1.95	2.59
1d	0.810	100	0.22	2.76	2.27	2.85
1d	1.07	100	0.22	2.91	2.48	2.94
1d	1.51	100	0.22	2.99	2.64	2.95
1d	3.02	100	0.22	2.75	2.66	2.68
1d	7.43	100	0.22	2.08	2.17	2.04

^a At 32.1 °C. ^b From conductivity measurements. ^c The $k'_{\text{calc}}k_w^{-1}$ values were calculated from eq 2 and 5, with $K_{\text{OH/Br}} = 0.04$ and $\alpha = 0.25$. The $k'_M(k_w\bar{V})^{-1}$ and K' values were taken from Table IV. Similarly, the $k_{\text{calc}}k_w^{-1}$ values were obtained on the basis of $k'_M(k_w\bar{V})^{-1}$ and K_S . ^d In the presence of 164 mM NaBr.

values for 1a (Table V). This can be rationalized in terms of a stabilization of the micelles in the presence of relatively high electrolyte concentrations, counteracting the interference by the sulfonate molecules with the micellization process (vide supra).²⁴

In the case of increasing bromide ion concentrations (Table V, entry 12), the PPIE model correctly predicts a rate inhibition of the biomolecular reaction. Such a complete inversion of the micellar rate effect induced by added electrolytes is only scarcely encountered.^{16,25}

One of the most intriguing parameters which can be calculated from $k'_M(k_w\bar{V})^{-1}$ is the true micellar rate effect k'_M/k_w^{-1} . Within the framework of the prolate ellipsoidal micelle model Bunton²⁶ has estimated the partial molar volume of micellized detergent monomer which contributes to the Stern layer ($\bar{V} = 0.14$ M⁻¹). We have adopted this value to calculate the k'_M/k_w^{-1} values for 1a–g (Table VI). Generally, the second-order rate constants are substantially (4–12 times) decreased in the micellar pseudophase as compared with those in water. Thus, the PPIE analysis confirms the dominant influence of the concentration effect,² which is completely responsible for the observed rate acceleration in the presence of micellar CTAB.

We will now briefly examine the modulation of the substituent effects of X and Y in the micellar solutions. This can be done at least in two ways. Firstly, k_{exp} values obtained at sufficiently high CTAB (>5 mM) concentration can be employed. Under these conditions the fraction

(21) The uncertainties in $K_{\text{OH/Br}}$ and α cannot account for the deviations at low detergent concentrations.

(22) These effects are calculated according to the procedure suggested in Shirama, K. *Bull. Chem. Soc. Jpn.* 1974, 47, 3165.

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(24) The cooperativity model⁴ can best describe these effects.

(25) The effect has also been found for a unimolecular reaction involving a charged substrate: Rupert, L. A. M.; Engberts, J. B. F. *N. J. Org. Chem.* 1982, 47, 5015.

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Table VI. Comparison of the Second-Order Rate Constants in the Micellar and Aqueous Pseudophases^a

compd	σ_p^b	$10^2 k_{\text{exp}}$, M ⁻¹ s ⁻¹	$k_M (k_w \bar{V})^{-1}$, mM	$10^3 k_M \bar{V}^{-1}$, s ⁻¹	$10^4 k_M'$, M ⁻¹ s ⁻¹	$10^4 k_w$, M ⁻¹ s ⁻¹	$k_w k_M'^{-1}$
1a	0.78	1290	2000	1260	1764	6300	4
1b	0.78	16.1	800	16.0	22.4	200	9
1c	0.00	8.9	600	8.10	11.3	135	12
1d	-0.17	4.2	670	3.92	5.49	58.5	11
1e	0.23	44	1000	37.1	51.9	371	7
1f	0.23	9.0	875	18.9	12.5	102	8
1g		10.5	c	8.07 ^d	11.3	c	

^aThe k_{exp} values (if necessary, interpolated) refer to [CTAB] = 5 mM, [NaOH] = 5 mM, and 32.1 °C. ^bHammett substituent constants refer to X (1b, 1f, 1d) or to Y (1a, 1c-e). ^cThis parameter could not be determined because of the low solubility of 1g. ^dCalculated from k_{exp} assuming that 1g was completely bound to the micelles.

Table VII. Comparison of Hammett Reaction Constants (ρ) for the Reaction of 1a-f with Hydroxide Ion in Water, CTAB Micelles, and 1,4-Dioxane-Water ($n_{\text{H}_2\text{O}} = 0.85$)^a

system	ρ	$-\log k_0$	r	p
w _X	0.56	2.13	0.9994	3
M _X	0.63	3.11	0.9822	3
m _X	0.60	1.24	0.9866	3
dw _X	0.76	2.95	0.9977	3
w _Y	2.14	1.88	0.9995	4
M _Y	2.69	2.88	0.9984	4
m _Y	2.66	0.98	0.9988	4
dw _Y	2.70	2.60	0.9995	4

^aLinear regression analysis of eight sets of second-order rate constants according to $\log k = \log k_0 + \rho \sigma_p$. Herein w refers to the reaction in water (k_w ; 5 mM NaOH, 32.1 °C); m to the reaction in CTAB micelles (k_{exp} ; [CTAB] = [NaOH] = 5 mM, 32.1 °C), M to second-order rate constants (k_M) from the PPIE analysis (Table VII), and dw to the system 1,4-dioxane-H₂O (mole fraction $n_{\text{H}_2\text{O}} = 0.85$, [NaOH] = 0.1 or 0.5 M, 32.1 °C), see Table VIII. The parameters r and p denote the correlation coefficient and the number of data points, respectively.

of solubilized sulfonate (f_S) will be high (if $K_S = 3 \text{ mM}^{-1}$, $f_S > 0.93$). Then eq 2 can be simplified into eq 6 and k_{exp}

$$k_{\text{exp}} \approx f_{\text{OH}} k_M (C\bar{V})^{-1} \quad (6)$$

at the same hydroxide (5 mM) and detergent concentration is directly proportional to k_M . In the second procedure, the k_M' values, extracted from the PPIE analysis (Table VI), can be used. Correlations with Hammett σ_p substituent constants, employing both approaches are summarized in Table VII. It is evident that the reaction rates reveal an increased susceptibility for variation of the substituent Y in the micellar pseudophase. The increase of ρ_X is less pronounced and unfortunately the linearity of the Hammett plot is not good enough to attach much significance to this result.

In order to compare the micellar effects with microenvironmental effects on the rate constants by solvent changes, the reactions were also performed in 1,4-dioxane-water ($n_{\text{H}_2\text{O}} = 0.85$) mixtures (Table VIII). The $E_T(30)$ value²⁷ of this mixed aqueous solvent is rather similar to that of the micellar environment (see Experimental Section). In this medium of reduced polarity, the second-order rate constants are also decreased whereas the ρ_Y value is increased. Interestingly, if we assume a partial molar volume of 0.3 M⁻¹ instead of 0.14 M⁻¹ for the detergent in the micellar pseudophase, which, in fact, comprises the whole micelle as reaction volume, the second-order rate constants k_M and k_{dw} become about equal. The lowering of the polarity in the micellar medium can also be rationalized by viewing the Stern region as a concentrated (ca. 3 M) salt solution.²⁸

Table VIII. Second-Order Rate Constants for the Reaction of 1a-f with Hydroxide Ions in 1,4-Dioxane-Water at $n_{\text{H}_2\text{O}} = 0.85$ ^a

compd	$10^3 k_{\text{dw}}$, M ⁻¹ s ⁻¹	compd	$10^3 k_{\text{dw}}$, M ⁻¹ s ⁻¹
1a	317	1d	0.816
1b	3.85	1e	10.3
1c	2.82	1f	1.72

^aAt 32.1 °C. [NaOH] = 0.5 mM for 1b, 1d, 1e and 0.1 mM for 1a, 1c, and 1f.

We conclude that the overall micellar rate effects are determined by two opposing factors: an increase in effective reactant concentration in the micellar pseudophase (at not too high detergent concentrations) and a lowering of the intrinsic rate constant in the less polar environment.

The possible occurrence of an orientational effect (depending on the nature of X and Y) upon binding of 1a-g in the Stern region of the CTAB micelles would lead to a modification of the catalytic effects not easily attainable in mixed aqueous solvents. If this were the case, the rate constants should be dissected into two rate constants, $k_{m,X}$ and $k_{m,Y}$, for each substrate binding mode. A similar dissection would also apply for the binding constants for the binding modes X and Y. Kinetic analysis¹ reveals that such orientational effects are then manifested in the magnitude of the average micellar rate constants (k_m) and not in the overall binding constant extracted from the kinetic data. However, we find that the micellar rate constants (k_{exp} ; k_m') correlate fairly well with σ_p and there is certainly no compelling reason for, for example, inclusion of a hydrophobicity parameter²⁹ in the correlation analysis. Apparently, there is only a minor limitation in the degrees of freedom of the sulfonate solubilized in the micelle, consistent with binding in the water-penetrated, open-channeled area of the outer Stern region.³⁰ Previously, evidence has been gathered that molecules containing aryl moieties are preferentially sorbed within the outer portion of the micelle.³¹ We submit that binding of the sulfonates 1a-g occurs at a rough micellar surface with the aryl groups floating like buoys on a turbulently surfaced ocean.

Experimental Section

Materials. The sulfonates 1a-g were prepared by the method of Bruggink.^{11,12a} CTAB was purified as described by Duynstee and Grunwald.³² 1,4-Dioxane was filtered through active neutral alumina. Sodium hydroxide and bromide (Merck) were of the highest grade available and were used as such. The water used

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in the kinetic experiments was demineralized and distilled twice in an all-quartz distillation unit. All solutions were made up by weight. The sodium hydroxide concentrations were determined (before addition of CTAB) by titration with $\text{KH}(\text{IO}_3)_2$.

Sulfonate **1f** was obtained from (*p*-chlorophenylsulfonyl) diazomethane.^{11,12a} A sample showed mp 134.5–135.0 °C; ¹H NMR (CDCl_3) δ 2.50 (2, 3 H), 4.95 (s, 2 H), 7.30–8.10 (m, 8 H). Anal. Calcd for $\text{C}_{14}\text{H}_{13}\text{ClO}_5\text{S}_2$: C, 46.60; H, 3.61. Found: C, 46.4; H, 3.6. The exact mass measured was in accord with a fragmentation leading to the loss of CH_2O from the molecular ion.³³

Kinetic Measurements. Reaction rates were determined under pseudo-first-order conditions by following the change of absorbance at 235 nm. The reactions were carried out in quartz cells placed in thermostated cell compartments of a Zeiss PMQII or a Cary Model 210 spectrophotometer. Relatively fast reactions (at higher NaOH concentration) were followed by using an Aminco-Morrow stopped-flow apparatus, equipped with a single-beam monochromator and a data acquisition storage and retrieval (DASAR) system. The optical path length of the thermostated mixing chamber was 1.0 cm. All rate constants were reproducible to within 2%. Calculations were performed by using an HP 25 programmable calculator.

Cmc Measurements. The cmc values (32.1 °C) were obtained from plots of specific conductivity ($\Omega^{-1} \text{cm}^{-1}$) vs. total CTAB concentration. A Wayne Kerr Autobalance Universal Bridge B642 fitted with a Philips electrode PW9512/01 (cell constant 0.71 cm^{-1})

was used. The following linear relations³⁴ were found:

$$\log \text{cmc} = -4.013 - 0.355 \log (\text{cmc} + [\text{NaOH}]) \quad (7)$$

$$\log \text{cmc} = -5.0966 - 0.588 \log (\text{cmc} + [\text{NaBr}]) \quad (8)$$

Equation 7 refers to the system (CTAB + NaOH) with [NaOH] ranging from 2 mM to 0.1 M. Equation 8 describes the cmc for mixtures of 5 mM NaOH, CTAB, and [NaBr] between 0 and 6 mM.

$E_T(30)$ Measurements. The $E_T(30)$ probe (2,4,6-triphenyl-*N*-[3,5-diphenyl-4-hydroxyphenyl]pyridinium betaine, kindly supplied by Prof. Ch. Reichardt, University of Marburg) dissolved in 0.1 M CTAB (25 °C) revealed $\lambda_{\text{max}} = 542 \text{ nm}$, corresponding with $E_T(30) = 52.8 \text{ kcal mol}^{-1}$. For 1,4-dioxane-water ($n_{\text{H}_2\text{O}} = 0.85$),²⁷ $E_T(30) = 54.2 \text{ kcal mol}^{-1}$.

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Registry No. **1a**, 31081-12-6; **1b**, 31081-08-0; **1c**, 31081-09-1; **1d**, 14894-58-7; **1e**, 31081-11-5; **1f**, 91817-01-5; **1g**, 62586-47-4; CTAB, 57-09-0; SDS, 151-21-3; NaOH, 1310-73-2; OH^- , 14280-30-9.

Supplementary Material Available: Second-order rate constants for the reaction of **1a–g** with hydroxide ion in the presence of CTAB micelles (Table IX) and the derivation of eq 5 (4 pages). Ordering information is given on any current masthead page.

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Gas-Phase Elimination Kinetics of (Dimethylamino)alkyl Acetates. The Ion-Pair Mechanism through Neighboring Group Participation

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The gas-phase elimination kinetics of some amino esters and a keto acetate have been studied in the temperature region of 260.0–411.5 °C and in the pressure range of 21.5–170.0 torr. These eliminations, in vessels seasoned with allyl bromide, are predominantly unimolecular and homogeneous and obey a first-order rate law. The rate coefficients for the reactions are expressible by the following Arrhenius equations: for 3-(dimethylamino)-1-propyl acetate (**1**), $\log k_1 (\text{s}^{-1}) = (12.97 \pm 0.20) - (202.1 \pm 2.5) \text{ kJ mol}^{-1} (2.303RT)^{-1}$; for 4-(dimethylamino)-1-butyl acetate (**4**), $\log k_1 (\text{s}^{-1}) = (11.91 \pm 0.43) - (163.5 \pm 4.8) \text{ kJ mol}^{-1} (2.303RT)^{-1}$; for 4-oxo-1-pentyl acetate (**7**), $\log k_1 (\text{s}^{-1}) = (12.77 \pm 0.36) - (202.8 \pm 4.6) \text{ kJ mol}^{-1} (2.303RT)^{-1}$. The presence of the $(\text{CH}_3)_2\text{N}$ group in these acetates appears to provide anchimeric assistance in the elimination; methyl acetate and the corresponding heterocyclic products arise from an intimate ion-pair mechanism. The CH_3CO substituent is believed to influence the pyrolysis rate of 5-acetoxy-2-pentanone by a weak steric acceleration.

In the past few years, our laboratory has aimed at demonstrating an intimate ion-pair-type of mechanism in the gas-phase elimination of organic molecules. Maccoll and Thomas¹ have already proposed this type of intermediate for alkyl halides and carboxylic esters pyrolyses. In this respect, we have assumed^{2,3} that such intermediates may likely occur if certain atoms within the same molecule can stabilize the reaction center in the transition state. Such a stabilization can possibly be accomplished through neighboring group participation. That is, the participation of a substituent may in some cases form an irreversible or real bond whereby an atom or group of atoms possibly

migrate or rearrange through intramolecular solvation or "autosolvation" by an intimate ion-pair mechanism. This type of intermediate appears to find support from two recent works on the gas-phase elimination of methyl esters of ω -chloro carboxylic acids³ and ethyl 4-bromobutyrate.² The formation of the corresponding lactone through rearrangement suggested that intimate ion pair mechanism by the anchimeric assistance of the COOCH_3 and $\text{COO-CH}_2\text{CH}_3$ substituents.

No homogeneous gas-phase study of rearrangement in ester pyrolysis has been reported, aside from a single case of rate enhancement in $\text{CH}_3\text{SCH}_2\text{CH}_2\text{OAc}$ through neighboring group participation of the CH_3S group.⁴ Therefore, the present work is addressed to study the

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