through "molecular lines of force", the simple recognition[14] of the alternate charge relay effect described by Pople and Gordon[42] seems adequate to account for gross effects at both α- and β-carbon atoms.

Conclusions

The findings reported here are based on an extensive set of substituents that exceeds the requirements for a minimal set to test correlative ability.[19,22] Although a set of substituent constants similar to σ^+ values can be devised to give the best correlations with SCS at the β-carbon atom, these constants fail completely when applied to SCS data at the α-carbon. The DSP approach is therefore mandated. A comparison of currently existing parameters for DSP treatments showed that both the Taft and Swain approaches gave very good results for the β-carbon data. In fact, for the substituents employed, Taft's $\sigma_R^\pm$ scale (σ_R^+ for electron donors and σ_R^- for electron withdrawers) correlates reasonably well with Swain's R values. The correlation between σ_I and F is unsatisfactory if the dimethylamino and phenyl groups are included, but excellent if they are excluded. Swain's parameters are definitely superior for the α-carbon data, where electronic effects are largely (80%) inductive. These results suggest that multiple resonance scales may be unnecessary and, possibly, that the Swain and Taft parameter sets would give nearly identical results if σ_I and F were more nearly parallel. The discrepancy seems to be in the σ_I value for either the dimethylamino or phenyl group, or both.

Acknowledgment. C.D.S. thanks Profs. F. H. Dietrich, Jr., and J. E. McKenney for helpful discussions.

Supplementary Material Available: Tables giving the chemical shifts for β-carbon atoms (S-I) in all series and for α-carbon atoms (S-II) in the para-substituted series, and adjusted correlation coefficients, $\bar{R}^2$, for correlations of shifts for β-carbon atoms in each para-substituted series (S-III) and meta-substituted series (S-IV) with various DSP treatments (4 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. 2.[1] The Absence of Substrate Orientational Effects in a Series of Sulfonates of Different Hydrophobicities

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Second-order rate constants for nucleophilic attack of hydroxide ion at the sulfonate sulfur atom of a series of sulfonates $R_1SO_2CH_2OSO_2R_2$ (**1a–g**) in the presence of CTAB micelles (at 50 °C) have been analyzed in terms of the pseudophase ion-exchange (PPIE) model. It is shown that the catalysis by the micelles is caused by the increased reactant concentrations in the micellar reaction volume. Large variations in the hydrophobicities of the substituents R_1 and R_2 (alkylaryl, alkyl) had only a minor influence on the rate constant for reaction in the micellar pseudophase (k_m). The same conclusion holds if the rate constants k_m are corrected for the different propensities of the sulfonates to respond to changes in the polarity of the reaction medium as expressed in the dielectric constant. Therefore there is no evidence that the depth of penetration and/or the orientation of the sulfonates **1a–g** bound to the cetyltrimethylammonium bromide micelles is significantly affected by the hydrophobicities of R_1 and R_2. These findings are reconcilable with recent views concerning the morphology of micelles.

The rates of a large variety of chemical reactions in aqueous solution are influenced by the presence of micelles.[2] The magnitude of the catalysis (or inhibition) depends crucially on the efficiency of micellar incorporation of the reactant(s) and on the effect of the specific microenvironment at the micellar binding sites, usually located at the micellar surface. In the case of bimolecular reactions, two reactants should bind to the micelle. This may lead to locally increased reactant concentrations and concomitant increased reactivity even if the rate constant in the micellar pseudophase is decreased relative to that in aqueous solution. Among the various kinetic treatments advanced for the analysis of catalysis by ionic micelles of bimolecular reactions involving a neutral reactant and hydrophilic reactant counterions, the pseudophase ion-exchange (PPIE) model[3] is one of the most successful approaches. But a quantitative analysis of the micellar rate effects is still hampered by several problems including the question of the constancy of counterion binding[4] and the choice of the volume element for reaction in the micellar pseudophase.[5] Mechanistically, the development of a clear picture of micellar catalytic effects hinges also on the availability of a realistic model for the morphology of ionic micelles. Although one should recognize the

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[5] Bunton, C. A.; Carrasco, M.; Huang, S. K.; Paik, C. H.; Romsted, L. S. *J. Am. Chem. Soc.* **1978**, *100*, 5420.

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possibility that reactant binding partly affects micellar structure,[6] interpretations of micellar rate effects should take into account the details of chain packing and counterion binding in the ionic micelles. Much current research is concerned with the structure of micelles.[7]

In the present study, primarily aimed at the elucidation of the effect of substrate hydrophobicity on micellar catalytic efficiency, we have determined rate constants for the reaction of the sulfonylmethyl sulfonates **1a–g** with hydroxide ions in the presence of cetyltrimethylammonium bromide (CTAB) micelles.

$$\underset{\mathbf{1}}{R_1SO_2CH_2OSO_2R_2} + 2OH^- \rightarrow R_1SO_2^- + CH_2O + R_2SO_3^- + H_2O \quad (1)$$

a, $R_1 = R_2 = p\text{-}CH_3C_6H_4$

b, $R_1 = p\text{-}CH_3C_6H_4$; $R_2 = p\text{-}CH_3(CH_2)_3C_6H_4$

c, $R_1 = p\text{-}CH_3C_6H_4$; $R_2 = p\text{-}CH_3(CH_2)_7C_6H_4$

d, $R_1 = p\text{-}CH_3C_6H_4$; $R_2 = CH_3$

e, $R_1 = p\text{-}CH_3C_6H_4$; $R_2 = CH_3(CH_2)_3$

f, $R_1 = p\text{-}CH_3C_6H_4$; $R_2 = CH_3(CH_2)_7$

g, $R_1 = CH_3(CH_2)_7$; $R_2 = p\text{-}CH_3C_6H_4$

Previous studies have shown that the reaction of sulfonates of type **1** with hydroxide ions involves nucleophilic attack of OH^- at the sulfonate sulfur atom with considerable bond making in the transition state.[8] A subsequent study revealed that the reaction of (arylsulfonyl)alkyl arenesulfonates (**2**) with hydroxide ion is speeded by the presence of CTAB micelles.[1] Detailed kinetic analysis in

$$\underset{\mathbf{2}}{p\text{-}XC_6H_4SO_2CH(R_3)OSO_2C_6H_4Y\text{-}p}$$

terms of the PPIE model indicated that the rate acceleration (ca. 7–25 times at 32.1 °C) should be ascribed to the bringing together of the neutral and ionic reactants in the micellar reaction volume. Upon variation of the para-substituents X and Y (Me, Cl, NO_2) no evidence for orientational effects was found.[1] However, the substituent effects were modulated as compared with those in water as a result of the reduced micropolarity at the substrate binding sites in the Stern layer of the micelle.[1]

In the present series of sulfonates **1a–g** we have systematically varied the hydrophobicity of the alkyl substituents R_1 and R_2 at both ends of the molecule. The possibility was envisioned[9] that the sulfonate sulfur atom of **1a–g**, which is attacked by OH^- ion in the rate-determining step, would be positioned in a different fashion relative to the micellar surface depending on the penetration of R_1 and R_2 into the micellar core as determined by the hydrophobicities of these groups. To test this possibility, the kinetic data were analyzed in terms of the PPIE model.[3] Reaction rates were also measured in 1,4-dioxane–water mixtures[10] in order to probe the effect of a reduced polarity of the reaction medium on the reaction of the sulfonates.

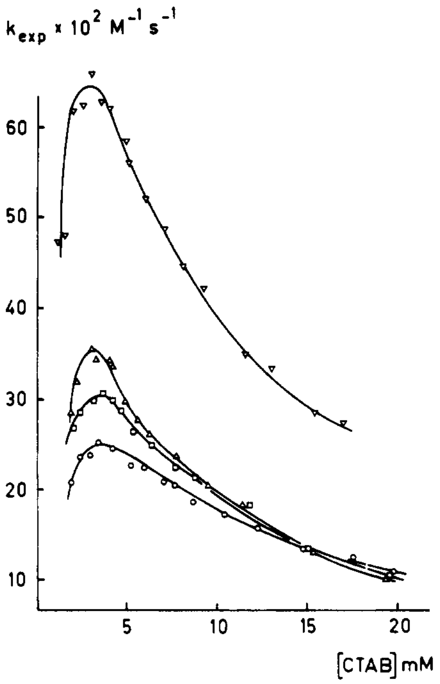

Figure 1. Plots of k_{exp} vs. [CTAB] for the reaction of the sulfonates **1a** (○), **1b** (□), **1c** (△), and **1g** (▽) with hydroxide ion at 50.0 °C and [NaOH] = 5 mM.

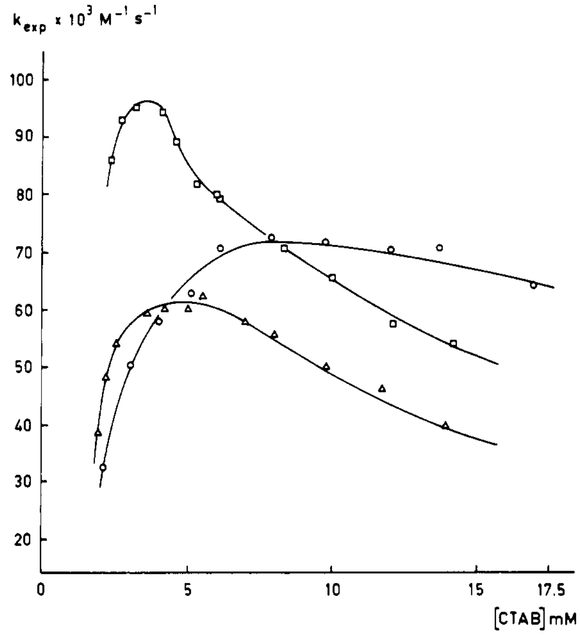

Figure 2. Plots of k_{exp} vs. [CTAB] for the reaction of the sulfonates **1d** (○), **1e** (△), and **1f** (□) with hydroxide ion at 50.0 °C and [NaOH] = 5 mM.

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[10] For a previous study of solvent effects, see: Holterman, H. A. J.; Engberts, J. B. F. N. *J. Phys. Chem.* **1979**, *83*, 443.

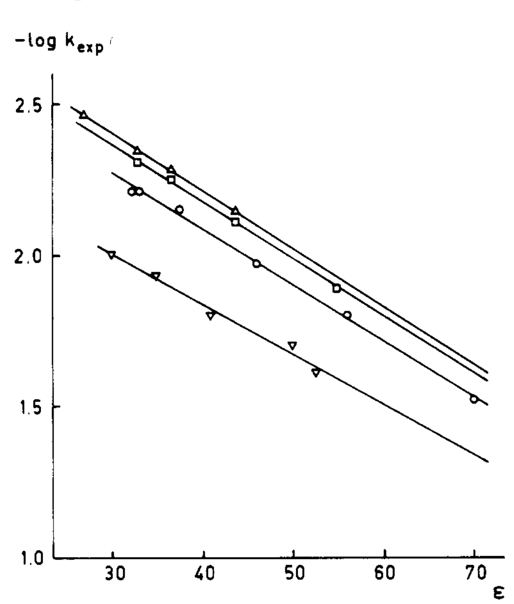

Figure 3. Plots of $-\log k_{exp}$ vs. dielectric constant (ϵ) for the reaction of the sulfonates **1a** (○), **1b** (□), **1c** (△), and **1g** (▽) with hydroxide ion in 1,4-dioxane–water at 50.0 °C and [NaOH] = 0.3 M.

Results and Discussion

The sulfonates **1a–g** were prepared by the reaction of the appropriate α-diazo sulfones with an arene- or alkanesulfonic acid (eq 2).[11] Reaction of **1a–g** with OH^- gave the expected sulfinate, sulfonate, and formaldehyde (eq 1).[8,11] Because of the limited solubility of the more hydrophobic sulfonates in water, all second-order rate constants for this reaction were measured at 50 °C. As anticipated,[1] the reactions are substantially accelerated in the presence of CTAB micelles. Second-order rate constants (k_{exp}) for the micellar-catalyzed reactions of **1a–g** as a function of [CTAB] at constant [OH^-] (5 mM) are listed in Table III (supplementary material) and are graphically displayed in Figures 1 and 2. These plots show the usual features for micellar-catalyzed bimolecular processes.[2] Below the critical micelle concentration (cmc; 7.2 × 10^{-4} M at 50 °C in the presence of 5 mM NaOH, see Experimental Section) there is hardly any effect on k_{exp}. An abrupt increase of k_{exp} occurs around the cmc. Then the rate constant passes through a maximum and gradually decreases at still higher concentrations of CTAB. We will analyze these data employing the PPIE model[3] in terms of structural effects on k_m (second-order rate constant for reaction in the micellar pseudophase) and k_w (second-order rate constant for reaction in water in the absence of detergent).

$$R_1SO_2CHN_2 + R_2SO_3H \rightarrow \underset{\mathbf{1a-g}}{R_1SO_2CH_2OSO_2R_2} + N_2 \quad (2)$$

Unfortunately no k_w values could be directly determined for the reactions of **1c**, **1f**, and **1g** because of their very low solubility in water even at 50 °C. To circumvent this problem, k_w values were measured as a function of solvent composition in not too water-rich 1,4-dioxane–water mixtures at 50 °C (Table IV, supplementary material). We find that not only for these sulfonates but also for those sulfonates sufficiently soluble to measure k_w (**1a**, **1d**, **1e**) there is an excellent linear relationship between log k_{exp} and the dielectric constant (ϵ).[12] The plots are shown in Figures 3 and 4. The fact that the plots are closely parallel within each series suggest that the solvent effects are not seriously complicated by preferential solvation of the more hydrophobic sulfonates by 1,4-dioxane.[13] Thus, we have extrapolated the log k_{exp} values for **1c**, **1f**, and **1g** to pure water (ϵ = 70 at 50 °C) to obtain probably accurate estimates of the respective k_w values.

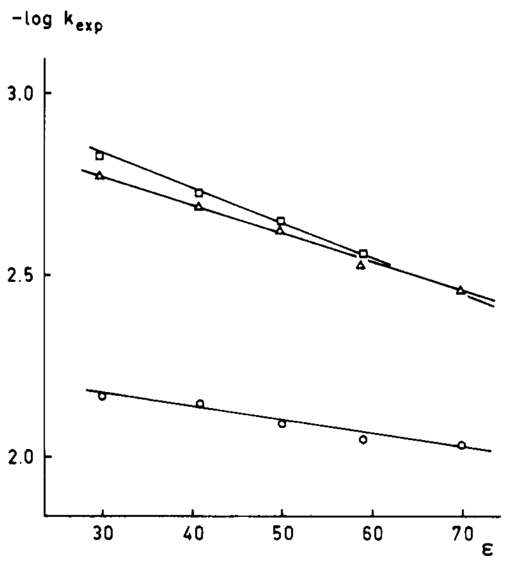

Figure 4. Plots of $-\log k_{exp}$ vs. dielectric constant (ϵ) for the reaction of the sulfonates **1d** (○), **1e** (△), and **1f** (□) with hydroxide ion in 1,4-dioxane–water at 50.0 °C and [NaOH] = 0.3 M.

The PPIE analysis proceeds essentially as described previously.[1] The basic kinetic equation is expressed in eq 3, in which f_s and f_{OH} are the fractions of sulfonate and OH^-, respectively, bound to the micelles and $C\bar{V}$ is the volume fraction of the reaction medium occupied by the micellar pseudophase.

$$k_{exp}k_w^{-1} = f_sf_{OH}k_mk_w^{-1}(C\bar{V})^{-1} + (1 - f_s)(1 - f_{OH}) \quad (3)$$

Herein C denotes the concentration of micellized detergent (C = [CTAB] − cmc) and $\bar{V}$ the partial molar volume of micellized CTAB molecules. The assumption that the counterion binding in the micelles is constant[3] can be expressed as

$$[OH]_m + [Br]_m = (1 - \alpha)C$$

in which $[OH]_m$ and $[Br]_m$ are the concentrations of OH^- and Br^- (with respect to the total solution volume) bound to the CTAB micelles and α is the total degree of ionization of the micelle. The ion-exchange constant is defined by eq 4, in which $[Br]_w$ and $[OH]_w$ are the concentrations of the respective ions not bound to the micelles.

$$K_{OH/Br} = \frac{[Br]_w[OH]_m}{[Br]_m[OH]_w} \quad (4)$$

The fraction of OH^- ions sorbed by the micelles (f_{OH}) can be obtained from the quadratic equation

$$f_{OH} = [OH]_m[OH]_t^{-1} = -B(2A)^{-1} + [B^2(2A)^{-2} - EA^{-1}]^{1/2} \quad (5)$$

in which

$$A = (1 - K_{OH/Br})$$

$$B = -E + K_{OH/Br} + \text{cmc}[OH]_t^{-1} + \alpha C[OH]_t^{-1}$$

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

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[11] Compare: Bruggink, A.; Zwanenburg, B.; Engberts, J. B. F. N. *Tetrahedron* **1970**, *26*, 4995.

[12] The physical significance of this correlation is uncertain, but this is unimportant for the present purpose.

[13] Compare: Remerie, K.; Engberts, J. B. F. N. *J. Phys. Chem.* **1983**, *87*, 5449 and references cited therein.

Table I. Sulfonate-CTAB Micellar Binding Constants K_s[a]

compd	Σf_i[b]	K_s, mM^{-1}
1a	0.7	3.3
1b	2.3	12
1c	4.4	70
1d	0.7	0.16
1e	2.3	0.60
1f	4.4	3.5
1g	4.4	3.5

[a] At 32 °C. [b] Σf_i *is the difference in* f_i *values*[16] *of the alkyl substituents in the sulfonates* **1a**–**1c** *and* **1d**–**1f**.

and $[OH]_t$ is the total concentration of OH$^-$ ions. The fraction of sulfonate bound to the CTAB micelles (f_s) can be defined in terms of a binding constant K_s. The appropriate relation is expressed in eq 6.

$$(1 - f_s) = (K_sC + 1)^{-1} \qquad (6)$$

Previously, the binding constant K_s has been determined for **1a** by using Thomapore tubular membranes.[1,14] Binding constants for **1d** and **1e** were determined at 32 °C by the same procedure, and it is assumed that the K_s values are only slightly temperature dependent.[15] The other binding constants were estimated on the same basis as differences in hydrophobicity have been defined in terms of Rekker's hydrophobic fragmental constants (f_i).[16] Thus, **1e** has three methylene groups more than **1d**. Since $\log K_{1e} - \log K_{1d} = 0.58$, the contribution per CH$_2$ to K_s is 0.19. Therefore, $\log K_{1f} = \log K_{1b} + (4 \times 0.19) = 0.54$, and $K_{1f} = 3.5$ mM^{-1}. A similar procedure was applied for the estimation of the other binding constants (Table I).

The PPIE treatment[3] used to evaluate k_m values (eq 3) was only applied to those k_{exp} values which were obtained under conditions that the sulfonate is (almost) completely bound to the micelles. Then eq 3 can be simplified[1] into eq 7. Values of k_w and k_m for the reactions of **1a**–**g** are

$$k_{exp} = f_s f_{OH} k_m (C\bar{V})^{-1} \qquad (7)$$

listed in Table II. In all cases $k_m k_w^{-1} < 1$, indicating that the observed rate accelerations in the micellar solutions are purely the result of increased reactant concentrations in the micellar pseudophase. We contend that the values of $k_m k_w^{-1}$ cannot be directly related to the depth of penetration of the substrate reaction site into the micellar core, since the different sulfonates may react in a different way to changes in micropolarity upon binding to the micelle. Previous studies[17] have provided evidence that the dielectric constant at the CTAB micellar surface is ca. 30. Second-order rate constants (k_{dw}) in 1,4-dioxane–water at the solvent composition of this dielectric constant (mole fraction of water, $n_{H_2O} = 0.83$) are shown in the fifth column of Table II. Then the values of $k_{dw} k_w^{-1}$ (Table II) reflect the different sensitiveness for changes in polarity of the reaction medium in the reactions of **1a**–**g** with OH$^-$ ions. Interestingly, $k_{dw} k_w^{-1}$ values are almost equal for those sulfonates in which an aryl ring is attached to the sulfonate sulfur atom and significant changes in this parameter do only occur for **1d**–**f** with R$_2$ = alkyl, i.e., in those sulfonates in which the substituent directly attached to the reaction center is varied. The last column in Table II shows values of $k_m k_{dw}^{-1}$ for **1a**–**g**. Although no solvent or solvent mixture will exactly mimic the microenvironment at micellar solubilization sites, we suggest that the magnitude of $k_m k_{dw}^{-1}$ is at least an approximate measure for the position of the sulfonate group (the reaction site in **1a**–**g**) relative to the micellar surface, as affected by the hydrophobicities of the substituents R$_1$ and R$_2$. In this context we note that the polarity and hydrogen-bonding ability of the sulfonyl[18] and sulfonate[19] moieties are very similar.

The most significant conclusion that can be drawn from the data in Table II is that the differences in $k_m k_{dw}^{-1}$ between the seven sulfonates are relatively small despite large variation in the hydrophobicities of R$_1$ and R$_2$. It seems clear that the aromatic rings are of paramount importance in determining the locus of the sulfonate molecule in the micelle. Previously, it has been shown that phenyl rings have a preference for binding at the micellar surface.[1,20–24] Within the series **1a**–**c** there is only a small increase of $k_m k_{dw}^{-1}$ upon increasing the hydrophobicity of the alkyl substituent R$_2$ which is directly bound to the reaction centre. Thus, the expectation that the sulfonate group would be drawn into the micellar core by a sufficiently hydrophobic substituent R$_2$ is not borne out by experiment. Comparison of the $k_m k_{dw}^{-1}$ values for **1f** and **1g**, two sulfonates of the same overall hydrophobicity but containing an *n*-octyl or *p*-tolyl group in the sulfonate part of the molecule, also shows a rather small difference. This is indicative for a similar position of the reaction site within the micellar aggregate. Quite unexpectedly, the smallest value of $k_m k_{dw}^{-1}$ is observed for **1d**, the least hydrophobic of the sulfonates examined in this study (smallest K_s value, Table I). This finding is primarily caused by the relatively large value of $k_{dw} k_w^{-1}$ (Table II, largest value of k_{dw}). The latter parameter decreases significantly in the series **1d**–**f** and illustrates the effect of chain length of the R$_2$ group directly attached to the sulfonate reaction site (vide supra). Such an effect is not found for the R$_1$ substituent as shown by the similar values of $k_{dw} k_w^{-1}$ for **1a** and **1g**.

In summary, the results of the present study clearly show that the relation between substrate structure and micellar kinetic effects cannot be simply couched in terms of changes in depth of substrate penetration into the micellar core as induced by variation of the hydrophobicity of the substrate. This conclusion holds for a bimolecular reaction involving hydroxide anion as the second reaction partner and which necessarily stays in the polar micelle–water interface. We submit that these results are not easily reconcilable with the classical Hartley micelle (oil drop with a polar coat).[2] Instead, the results seem to suggest that an uncharged, hydrophobic substrate binds onto the micelle rather than into the micelle, thereby keeping its reaction site exposed to reactant ions in the innermost part of the electrical double layer. This view implies that there are hydrophobic binding sites at the micellar surface. Interestingly, this is in keeping with modern theories regarding micellar structure, which assume that appreciable hydrocarbon segments of the detergent molecules in the

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Table II. Kinetic Data for the CTAB-Catalyzed Reaction of 1a–g with Hydroxide Ion at 50 °C. Analysis according to the PPIE Model[a] and Comparison with the Reaction in 1,4-Dioxane–Water (n_{H_2O} = 0.83)[b]

compd	$10^3 k_w$, $M^{-1}\ s^{-1}$	$10^3 k_m$, $M^{-1}\ s^{-1}$	$k_m k_w^{-1}$	$10^3 k_{dw}$,[d] $M^{-1}\ s^{-1}$	$k_{dw} k_w^{-1}$ [e]	$k_m k_{dw}^{-1}$ [f]
1a	25	3.5	0.14	5.4	0.18	0.8
1b	21[c]	3.7	0.18	4.3	0.17	1.0
1c	19[c]	3.8	0.20	4.0	0.18	1.1
1d	8.2	2.2	0.27	6.3	0.67	0.4
1e	3.0	1.1	0.37	1.5	0.41	0.85
1f	3.1[c]	1.2	0.39	1.3	0.35	1.1
1g	39[c]	7.0	0.18	10	0.22	0.8

[a] Binding constants are given in Table I. Second-order rate constant for the reaction in water is k_w and in the micelle k_m. [b] Second-order rate constant in 1,4-dioxane–water at n_{H_2O} = 0.83 is k_{dw}. [c] Rate constant determined via extrapolation of the rate constants in 1,4-dioxane–water (see text). [d] Rate constants determined in the presence of 0.3 M NaOH. [e] Calculated using k_w values determined in the presence of 0.3 M NaOH. [f] Calculated from $k_m k_w^{-1}$ $(k_{dw} k_w^{-1})^{-1}$.

micelle are exposed to water.[7b–f]

Experimental Section

Melting points were determined on a Mettler FP1 melting point apparatus. ^1H NMR spectra were measured at 60 MHz on a Hitachi Perkin-Elmer R-24B instrument. Chemical shifts in chloroform-*d* solutions are reported in δ units relative to internal Me_4Si. Infrared spectra were measured on a Unican SP-200 instrument. Elemental analyses were performed by H. Draayer, J. Ebels, and J. E. Vos of the analytical section of this department.

Materials. The sulfonates **1a–g** were synthesized by the method of Bruggink.[11] The required α-diazo sulfones were prepared as described by Van Leusen and Strating.[25] The anhydrous sulfonic acids[26] were obtained from the corresponding sodium sulfonates by passing an aqueous solution through a Dowex 50W, X8 20–50 mesh (Fluka) column. Evaporation of the solvent provided the sulfonic acids, which were characterized by their melting points (except one) and their ^1H NMR and IR spectral data. The mass spectra of the new sulfonates all showed a characteristic loss of a CH_2O fragment from the molecular ion.[27] *n*-Octanesulfonic acid was obtained as an oil and used immediately in the reaction with the α-diazo sulfone. The sulfonates **1a**[1] and **1d**[8] have been described previously.

(*p*-Tolylsulfonyl)methyl *p*-butylbenzenesulfonate (1b): yield 44%; mp 64.3–64.7 °C (from methanol); ^1H NMR δ 0.8–1.1 (m, 3 H), 1.1–1.8 (m, 4 H), 2.42 (s, 3 H), 2.50–2.85 (t, 2 H), 4.85 (s, 2 H), 7.15–7.75 (m, 8 H); IR (KBr) 1150, 1180, 1195, 1305, 1315, 1335 cm^{-1}. Anal. Calcd for $C_{18}H_{22}O_5S_2$: C, 56.53; H, 5.80; S, 16.76. Found: C, 56.41; H, 5.85; S, 16.82.

(*p*-Tolylsulfonyl)methyl *p*-octylbenzenesulfonate (1c): yield 63%; mp 52.4–52.8 °C (from methanol); ^1H NMR δ 0.8–1.1 (m, 3 H), 1.1–1.8 (m, 12 H), 2.42 (s, 3 H), 2.45–2.80 (t, 2 H), 4.75 (s, 2 H), 7.10–7.65 (m, 8 H); IR (KBr) 1160, 1175, 1195, 1310, 1325, 1340 cm^{-1}. Anal. Calcd for $C_{22}H_{30}O_5S_2$: C, 60.25; H, 6.89; S, 14.62. Found: C, 60.26; H, 6.97; S, 14.64.

(*p*-Tolylsulfonyl)methyl *n*-butanesulfonate (1e): yield 60%; mp 94.8–95.5 °C (from 90% (v/v) MeOH–H_2O); ^1H NMR δ 0.85–1.10 (m, 3 H), 1.10–2.05 (m, 4 H), 2.42 (s, 3 H), 3.05–3.40 (s, 2 H), 4.95 (s, 2 H), 7.20–7.80 (dd, 4 H); IR (KBr) 1155, 1175, 1310, 1320, 1340, 1360 cm^{-1}. Anal. Calcd for $C_{12}H_{18}O_5S_2$: C, 47.04; H, 5.92; S. 20.93. Found: C, 47.33; H, 5.97; S, 20.88.

(*p*-Tolylsulfonyl)methyl *n*-octanesulfonate (1f): yield 36%; mp 51.1–51.4 °C (from 90% (v/v) MeOH–H_2O); ^1H NMR δ 0.75–1.05 (m, 3 H), 1.05–2.00 (m, 12 H), 2.42 (s, 3 H), 3.05–3.30 (t, 2 H), 4.90 (s, 2 H), 7.15–7.80 (dd, 4 H); IR (KBr) 1160, 1170, 1310, 1325, 1345, 1375 cm^{-1}. Anal. Calcd for $C_{16}H_{26}O_5S_2$: C, 53.01; H, 7.23; S, 17.69. Found: C, 52.99; H, 7.12; S, 17.60.

(*n*-Octylsulfonyl)methyl *p*-toluenesulfonate (1g): yield 45%; mp 59.8–60.4 °C (from 90% (v/v) MeOH–H_2O); ^1H NMR δ 0.8–1.1 (m, 3 H), 1.1–2.0 (m, 12 H), 2.43 (s, 3 H), 2.9–3.2 (t, 2 H), 4.70 (s, 2 H), 7.2–7.8 (dd, 4 H); IR (KBr) 1150, 1185, 1200, 1310, 1325, 1340, 1375 cm^{-1}. Anal. Calcd for $C_{16}H_{26}O_5S_2$: C, 53.01; H, 7.23; S, 17.69. Found: C, 53.12; H, 7.22, S, 17.57.

Kinetic Measurements. CTAB (Merck) was purified as described by Duynstee and Grunwald.[28] 1,4-Dioxane (Merck, pro analysi) was filtered through active neutral alumina and stored at −20 °C. Sodium hydroxide (Merck) was of the highest grade available and was used as such. The water used 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 and after mixing with 1,4-dioxane, respectively) by titration with $KH(IO_3)_2$. Fresh solutions were used in the measurements.

Reaction rates were determined as described previously[1] by following the changes of absorbance at 235 nm on a Cary Model 210 spectrophotometer. Starting concentrations of the sulfonates were ca. 10^{-5} M. The rate constants were reproducible to within 2%.

The rate constants in 1,4-dioxane–water (Table IV, supplementary material) were determined at NaOH concentrations higher than 5 mM (concentration used in the micellar solutions) in order to avoid too long half-lives. Rate constants determined for **1b**, **1c**, **1f**, and **1g** between 5 mM and 0.3 M showed that plots of pseudo-first-order rate constants vs. [NaOH] deviate somewhat from linearity at the higher NaOH concentrations.[29] Since the corrections were the same for these sulfonates in order to place the rate constants on the linear relation in the low concentration range, the same correction factor was applied for **1a**, **1d**, and **1e** to obtain the rate constants at 5 mM NaOH and, ultimately, the k_w values (Table II).

Cmc Measurements. The cmc values of CTAB were determined from plots of specific conductivity (Ω^{-1} cm^{-1}) vs. total CTAB concentration. The conductivities were measured using a Wayne Kerr Autobalance Universal Bridge B642 fitted with a Philips electrode PW9512/01. At 50 °C we find cmc = 14.3 × 10^{-4} M (H_2O) and 7.2 × 10^{-4} M (5 mM NaOH).

Registry No. **1a**, 14894-58-7; **1b**, 97998-69-1; **1c**, 97998-70-4; **1d**, 62586-48-5; **1e**, 97998-71-5; **1f**, 97998-72-6; **1g**, 97998-73-7.

Supplementary Material Available: Rate constants for the reaction of **1a–g** with hydroxide ions in the presence of CTAB micelles (Table III) and rate constants for the same reaction in 1,4-dioxane–water mixtures in the absence of CTAB (Table IV) (5 pages). Ordering information is given on any current masthead page.

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