# Micellar Effects upon Spontaneous and Carboxylate Ion Catalyzed Hydrolyses of Benzenesulfonyl Chlorides

Clifford A. Bunton,* Marutirao M. Mhala, and John R. Moffatt

*Department of Chemistry, University of California, Santa Barbara, California 93106*

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Spontaneous hydrolyses of benzenesulfonyl chlorides are inhibited by micelles of cetyltrimethylammonium chloride (CTACl), sodium dodecyl sulfate (SDS), and *N*-hexadecyl-*N*,*N*-dimethyl-3-ammonio-1-propanesulfonate (SB3-16). The rate constants for hydrolyses of fully bound substrates are similar in CTACl and SB3-16. The rate constants in CTACl ($k^+$) and SDS ($k^-$) depend on the electronic effects of the 4-substituents and $k^+/k^-$ increases in the sequence MeO < Me < H < Br < $NO_2$. These micellar charge effects are ascribed to changes in the extents of bond-making and -breaking in the transition state. Hydrolysis in micellized *N*-dodecyl-*N*,*N*-dimethylglycine (B1–12) is inhibited, but this effect is offset by nucleophilic participation by the carboxylate moiety. Electron-withdrawing substituents strongly favor nucleophilic participation and for the 4-bromo and 4-nitro derivatives second-order rate constants in zwitterionic betaine micelles of B1–12 are similar to those for reaction with nonmicellized *N*,*N*,*N*-trimethylglycine in water.

*Nucleophilic* attack upon a sulfur atom of a sulfonyl derivative or a sulfonate ester has been discussed in terms of either a synchronous $S_N2$-type or an addition–elimination mechanism.[1-4] For nonsolvolytic reactions there is considerable dependence upon both the reactivity of the attacking nucleophile and the ease of departure of the leaving group. We have much less evidence on the role of bond-making in solvolytic reactions, although all the evidence suggests that solvent molecules participate as nucleophiles in hydrolyses of sulfonyl chlorides, for example, and there is no evidence for an $S_N1$-like ionization.[1] Most reactions have been examined in organic or aqueous organic solvent mixtures.

**Table I. Reaction in Solutions of *N*,*N*,*N*-Trimethylglycine**[a]

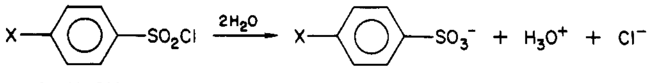
| [$Me_3{}^+NCH_2$-$CO_2{}^-$], M | substrate | | | | |
|---|---|---|---|---|---|
| | 4-MeO | 4-Me | 4-H | 4-Br | 4-$NO_2$ |
| | 61.0 | 38.6 | 30.7 | 19.6 | 24.5 |
| 0.01 | 61.8 | | | | |
| 0.05 | 61.7 | | 32.1 | 21.4 | |
| 0.075 | 64.1 | 39.2 | 32.6 | | 33.0 |
| 0.1 | 64.5 | 49.4 | 34.2 | 23.2 | 39.0 |
| 0.15 | | 48.2 | | 28.4 | 41.0 |
| 0.2 | 71.9 | 48.7 | 41.5 | 30.9 | 44.0 |
| 0.3 | 76.9 | | 51.3 | | |

[a] Values of $10^4 k_\psi$, $s^{-1}$, at 25.0 °C.

Ionic micelles generally inhibit spontaneous hydrolyses of acyl chlorides,[5,6] carboxylic anhydrides,[5,6] diaryl carbonates,[5,7] alkyl halides, and sulfonate esters.[5,7,8] The inhibition is understandable because all these reactions are inhibited by a decrease in the water content of a mixed solvent[9] and polarities at micellar surfaces appear to be lower than that of bulk water.[10] In addition micellar bound water may be less reactive than bulk water, although evidence is conflicting on this question.[11-14] Ionic micelles also appear to have an additional effect which is related to their charge.[5,6,8] Reactions in which bond-breaking dominates, e.g., $S_N1$-like reactions of alkyl halides, are faster in anionic than in cationic micelles, although they are slower than in water. Reactions in which bond-making dominates, e.g., hydrolyses of carboxylic anhydrides or diaryl carbonates are faster in cationic than in anionic micelles.

This test has been applied to hydrolyses of substituted benzoyl chlorides and aryl chloroformates.[5,6] Electron-withdrawing substituents, which should assist bond-making, speed hydrolyses in cationic relative to anionic micelles, but electron-donating substituents have the opposite effect.

To date this approach has not been applied to the attack of water upon heteroatoms, and we now apply it to spontaneous heterolyses of 4-substituted benzenesulfonyl chloride (1).



**1a**, X = OMe
**1b**, X = Me
**1c**, X = H
**1d**, X = Br
**1e**, X = $NO_2$

The cationic surfactant was cetyltrimethylammonium chloride (CTACl, $C_{16}H_{33}NMe_3Cl$), and the anionic surfactant was sodium dodecyl sulfate (SDS, $C_{12}H_{25}OSO_3Na$). We also used two zwitterionic surfactants, the sulfobetaine, *N*-hexadecyl-*N*,*N*-dimethyl-3-ammonio-1-propanesulfonate (SB3-16, $C_{16}H_{33}N^+Me_2(CH_2)_3SO_3^-$) and the betaine, *N*-dodecyl-*N*,*N*-dimetylglycine (B1-12, $C_{12}H_{25}N^+Me_2CH_2CO_2^-$), which has a potentially nucleophilic carboxylate ion at the head group. This nucleophilic attack

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(1) Kice, J. L *Adv. Phys. Org. Chem.* **1980**, *17*, 65.
(2) Ciuffarin, E.; Senatore, L.; Isola, M. *J. Chem. Soc., Perkin Trans. 2* **1972**, 468.
(3) Rogne, O. *J. Chem. Soc. B.* **1971**, 1855; *J. Chem. Soc., Perkin Trans. 2* **1972**, 472; **1975**, 1486.
(4) Strangeland, L. J.; Senatore, L.; Ciuffarin, E. *J. Chem. Soc., Perkin Trans. 2* **1972**, 852.
(5) Al-Lohedan, H.; Bunton, C. A.; Mhala, M. M. *J. Am. Chem. Soc.* **1982**, *104*, 6654.
(6) Bunton, C. A.; Mhala, M. M.; Moffatt, J. R. 5th Int. Symposium on Surfactants; Bordeaux, July, 1984.
(7) Menger, F. M.; Yoshinaga, H.; Venkatasubban, K. S.; Das, A. R. *J. Org. Chem.* **1981**, *46*, 415.
(8) Bunton, C. A.; Ljunggren, S. *J. Chem. Soc., Perkin Trans. 2* **1984**, 355.
(9) (a) Ingold, C. K. "Structure and Mechanism in Organic Chemistry", 2nd ed.; Cornell University Press: Ithaca, 1969; Chapter 7. (b) Johnson, S. L. *Adv. Phys. Org. Chem.* **1967**, *5*, 237.
(10) Cordes, E. H.; Gitler, C. *Prog. Bioorg. Chem.* **1973**, *2*, 1. Mukerjee, P. In "Solution Chemistry of Surfactants"; Mittal, K. L., Ed.; Plenum Press: New York, 1979; Vol. 1, p 153. Fernandez, M. S.; Fromherz, P. *J. Phys. Chem.* **1977**, *81*, 1755.
(11) Menger, F. M. *Acc. Chem. Res.* **1979**, *12*, 111.
(12) Bunton, C. A.; Huang, S. K. *J. Org. Chem.* **1972**, *37*, 1790.
(13) de Albrizzio, J. P.; Cordes, E. H. *J. Colloid Interface Sci.* **1979**, *68*, 292.
(14) van de Langkruis, G. B.; Engberts, J. B. F. N. *J. Org. Chem.* **1984**, *49*, 4152.

0022-3263/85/1950-4921$01.50/0

**Table II. Hydrolysis in Cationic and Anionic Micelles**[a]

| | substrate | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 4-MeO | | 4-Me | | 4-H | | 4-Br | | $4-NO_2$ | |
| [D], M | CTACl | SDS | CTACl | SDS | CTACl | SDS | CTACl | SDS | CTACl | SDS |
| 0.01 | | | | | | | | | 23.9 | |
| 0.05 | 3.78 | 6.20 | | | | | 5.28 | 2.35 | 23.4 | 5.16 |
| 0.075 | 2.54 | 4.17 | | | | | | | 23.3 | |
| 0.1 | 2.16 | 3.70 | 2.22 | 1.99 | 3.49 | 3.25 | 4.70 | 1.49 | 21.3 | 4.73 |
| 0.15 | 1.74 | 2.51 | | | | | 4.47 | 1.28 | 19.3 | 2.85 |
| 0.2 | 1.53 | 2.13 | 1.79 | 1.30 | | | | | | |
| 0.25 | | | | | 2.41 | 1.72 | | | 19.9 | 2.42 |
| 0.3 | 1.18 | 1.61 | | | | | 4.25 | 0.92 | | 2.36 |
| 0.35 | | | | | | | | | 22.1 | 1.81 |
| 0.4 | 1.18 | 1.42 | | | | | | | 22.2 | 1.64 |
| 0.5 | | | 1.36 | 0.78 | 1.90 | 0.90 | 4.26 | 0.80 | 22.8 | 1.65 |
| 0.6 | | | 1.25 | 0.63 | 1.99 | 0.78 | | 0.73 | | |
| 0.7 | | | 1.10 | 0.57 | 1.87 | 0.69 | 4.15 | 0.65 | | |
| 0.8 | | | 1.19 | 0.57 | 1.79 | 0.66 | | | | |

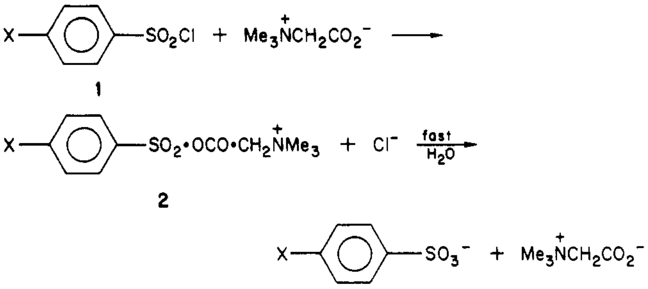
[a] Values of $10^4 k_\psi$, $s^{-1}$, at 25.0 °C.

in the micelle can be compared with reaction of *N,N,N*-trimethylglycine in water.

## Results and Discussion

The first-order-rate constants, $10^3 k_\psi$, $s^{-1}$, for the spontaneous hydrolyses of the following derivatives in water are the following: 4-MeO, 6.10; 4-Me, 3.86; 4-H, 3,07; 4-Br, 1.96; $4-NO_2$, 2.45. Substituent effects are small for hydrolysis in water with strongly electron-donating or -withdrawing groups slightly speeding reactions; cf. ref 1–4.

Reaction in water is speeded by *N,N,N*-trimethylglycine, but the rate enhancements are not large (Table I) as expected because the carboxylate ion is not a strong base[15] ($pK_a = 1.84$), and it should be a weak nucleophile. We saw no deviation from first-order kinetics in these reactions which suggests that the first formed mixed anhydrides (**2**) are rapidly hydrolyzed. Deacylations of betaine esters and related derivatives are generally faster than those of the otherwise similar nonionic compounds[16] and hydrolysis of **2** should be fast under the reaction conditions.



The rate enhancements are insensitive to electronic effects of substituents although electron-withdrawing groups appear to favor nucleophilic attack (Table I). However, $k_\psi$, does not increase linearly with $[Me_3^+NCH_2CO_2^-]$, suggesting that the betaine is exerting a medium effect as well as reacting nucleophilically. Such effects are understandable because a high concentration of betaine had to be used, and only with the bromo and nitro derivatives (**1d,e**) was it reasonable to estimate second-order rate constants for nucleophilic attack.

Spontaneous hydrolyses of the sulfonyl chlorides are inhibited by micelles of SDS, CTACl, and the zwitterionic sulfobetaine (SB3-16), and the increased reaction rate in solutions of the micellized nucleophilic betaine (B1-12) is almost certainly due to nucleophilic attack by the carboxylate moiety (Tables II–IV).

**Table III. Hydrolysis in Sulfobetaine Micelles**[a]

| | substrate | | | | |
|---|---|---|---|---|---|
| [D], M | 4-MeO | 4-Me | 4-H | 4-Br | $4-NO_2$ |
| | 61.0 | 38.6 | 30.7 | 19.6 | 24.5 |
| 0.003 | | | 16.5 | | |
| 0.005 | | | 15.9 | | |
| 0.01 | 8.24 | 5.91 | 8.0 | 5.75 | 23.2 |
| 0.02 | | | 5.8 | | |
| 0.03 | 3.68 | 3.28 | 5.3 | 4.28 | 23.0 |
| 0.04 | | | 4.2 | | |
| 0.05 | 2.71 | 2.39 | 3.8 | 3.98 | 22.7 |
| 0.075 | 2.13 | 1.89 | | 3.95 | 22.6 |
| 0.1 | | | | | 22.2 |
| 0.15 | | | | | 22.0 |

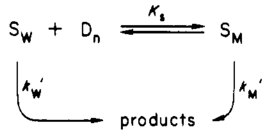
[a] Values of $10^4 k_\psi$, $s^{-1}$, at 25.0 °C.

**Table IV. Reaction in Zwitterionic Carboxylate Ion Micelles**[a]

| | substrate | | | | |
|---|---|---|---|---|---|
| [D], M | 4-MeO | 4-Me | 4-H | 4-Br | $4-NO_2$ |
| | 61.0 | 38.6 | 30.7 | 19.6 | 24.5 |
| 0.005 | 56.2 | | 32.4 | 85.9 | |
| 0.01 | 41.2 | | 43.9 | 189 | |
| 0.02 | 36.7 | | | 243 | |
| 0.03 | 34.0 | 49.7 | 58.4 | 280 | |
| 0.04 | 33.7 | | | 274 | |
| 0.05 | 32.4 | 51.4 | 68.0 | 276 | |
| 0.075 | 30.5 | 50.7 | 73.6 | | 1410 |
| 0.1 | 29.2 | 50.5 | 84.2 | 271 | 1600 |
| 0.15 | | 49.5 | 83.8 | | 2160 |
| 0.2 | 30.7 | 54.3 | | | 2650 |

[a] Values of $10^4 k_\psi$, $s^{-1}$, at 25.0 °C.

**Scheme I**



It is convenient to consider first hydrolyses in solutions of the nonnucleophilic surfactants,[17] and it is necessary to estimate the first-order rate constant, $k_M'$, for reaction of the micellar-bound substrate.

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(15) Dawson, R. M. C.; Elliott, D. C.; Elliott, W. H.; Jones, K. M. "Data for Biochemical Research"; Clarendon Press: Oxford, 1959.

(16) Bell, R. P.; Lindars, F. J. *J. Chem. Soc.* **1954**, 4601. Bell, R. P.; Collier, B. A. *Trans. Faraday Soc.* **1964**, 60, 1087.

(17) The sulfonate moiety should be too weakly nucleophilic to react with the substrates.

**Table V. Micellar Charge Effects**

| | substrate | | | | |
|---|---|---|---|---|---|
| | 4-MeO | 4-Me | 4-H | 4-Br | $4\text{-}NO_2$ |
| $10^4 k_{CTACl}$, $s^{-1}$ | 0.85 | 1.0 | 1.6 | 4.1 | 21 |
| $10^4 k_{SDS}$, $s^{-1}$ | 0.75 | 0.35 | 0.3 | 0.75 | 1.0 |
| $10^4 k^{SB}$, $s^{-1}$ | 0.85 | 1.0 | 1.5 | 3.6 | 22 |
| $k^+/k^-$ | 1.1 | 3 | 5 | 5 | 21 |
| $k^+/k^{SB}$ | 1.0 | 1 | 1 | 1.2 | 1 |
| $k^+/k^-$(ArCOCl)[a] | 0.1 | 0.2 | 0.6 | 5 | 12 |

[a] Reference 6.

Micellar effects upon spontaneous or micellar-inhibited nonsolvolytic reactions can be treated on the basis of Scheme I,[18] where $D_n$ is the micellized surfactant, $K_s$ a binding constant of substrate, S, and subscripts W and M denote aqueous and micellar pseudophases, respectively.

The variation of the overall rate constant with [surfactant] is given by

$$k_\psi = (k_W' + k_M'K_s([D] - \text{cmc}))/(1 + K_s([D] - \text{cmc})) \tag{1}$$

where the concentration of the monomeric surfactant is assumed to be given by the critical micelle concentration, cmc.[18]

Equation 1 can be rearranged into a reciprocal form, but it is unsatisfactory for estimating $k'_M$ if the reaction is strongly inhibited.[7,18] However, provided that the substrate is extensively micellar bound, $1 \ll K_s([D] - \text{cmc})$, and if $[D] \gg \text{cmc}$, eq. 1 gives

$$k_\psi = k_W'/K_s[D] + k'_M \tag{2}$$

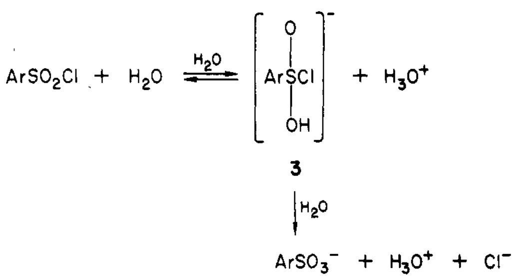
and $k_M'$ is given by extrapolation of a plot of $k_\psi$ against $1/[D]$.[8]

We denote values of $k_M'$ in CTACl, SDS, and the sulfobetaine (SB3-16) as $k^+$, $k^-$, and $k^{SB}$, respectively, and they are given in Table V. The low solubility of the sulfobetaine surfactant made it difficult to obtain good values of $k^{SB}$, except for hydrolysis of the nitro derivative where reaction is rapid and precipitation is not a problem. Values of $k^+/k^-$ are sensitive to the electronic effects of the 4-substituents but values of $k^+/k^{SB}$ are close to unity.

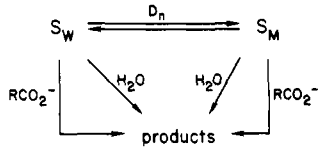
Substituent effects upon $k^+/k^-$ (Table V) are qualitatively similar to those observed for hydrolyses of benzoyl chlorides[5,6] except that with all the sulfonyl chlorides $k^+/k^- > 1$. These observations are consistent with the hypothesis that values of $k^+/k^-$ are related to the relative extents of bond-making and -breaking in the transition state. If bond-making is significant, $k^+/k^- > 1$,[5] as is observed in hydrolyses of the sulfonyl chlorides. The values of $k^+/k^-$ increase with increasing electron withdrawal by the 4-substituent in the sequence MeO < H ~ Me < Br < $NO_2$. A plot of log $k^+/k^-$ against $\sigma_p$ is approximately linear with $\rho \approx 1.3$. This sequence is very similar to that for hydrolyses of benzoyl chlorides for which a plot of log $k^+/k^-$ against $\sigma$ gives $\rho \approx 2$.[6]

The electronic effects upon $k^+/k^-$ (Table V) are consistent with the hypothesis that micellar charge effects are related to extents of bond-making and -breaking in the transition state.[5,6,8] It is highly unlikely that spontaneous hydrolyses of arenesulfonyl chlorides or similar compounds follow a dissociative mechanism in aqueous media,[1] although bond-breaking seems to be of major importance in solvolyses of benzoyl chlorides in polar solvents, and some authors consider that hydrolysis can follow an $S_N1$ reaction, cf. ref 9b, 19. The results are also inconsistent with an addition–elimination mechanism in which substrate is converted completely into a hydrate (or its anion) which slowly loses chloride ion. However, reaction could involve formation of an intermediate which either returns to reactants or goes forward to product; alternatively, addition of water could be concerted with loss of chloride ion. The concerted mechanism seems more realistic from one point of view which is that hydrate intermediate would probably be a strong acid in water (Scheme II). In that event it would rapidly give the anion 3 which would readily lose $Cl^-$. Alternatively, water addition could be concerted with transfer as in many spontaneous hydrolyses of acyl derivatives.[20] In either event the transition state in water would have considerable anionic character, which is inconsistent with the small electronic effects in the reaction.

**Scheme II**



**Scheme III**[a]



[a] $R = Me_3{}^+NCH_2$ ; $R = C_{12}H_{25}{}^+NMe_2CH_2$.

Thus it seems reasonable to treat these hydrolyses as concerted additions of water and elimination of chloride ion and to assume that the relative importance of these two steps depends upon both substrate structure and reaction medium. For hydrolysis of the 4-nitro compound 1e in cationic micelles it appears that bond-making is dominant and that the structure of the transition state is similar to that of the hypothetical anionic intermediate 3, but that loss of $Cl^-$ becomes more important when electron-donating groups are present. It has been pointed out that nucleophilic attack upon sulfonyl halides and similar compounds differs from that upon benzoyl halides in that sulfur can readily increase its covalency and accommodate negative charge.[1,3] However, the small electronic effects upon the spontaneous hydrolysis in water suggests that this increase is small and much less than that associated with attack of stronger nucleophiles.

The sulfobetaine (SB3-16) forms a zwitterionic micelle with the anionic sulfonate group extending from the micellar surface into the water. If the substrate is located near the quaternary ammonium ions, it will be in an environment similar to that provided by a cationic micelle. In many respects the two systems should be similar in that for CTACl the extent of fractional charge neutralization, $\beta$, is ca. 0.7.[21] Thus zwitterionic micelles can be regarded as being similar to hypothetical cationic micelles for which $\beta = 1$, i.e., in which there is complete charge neutralization by bound counterions. Similar rate effects of sulfobetaine

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(18) Menger, F. M.; Portnoy, C. E. *J. Am. Chem. Soc.* **1967**, *89*, 4698.

(19) Bentley, T. W.; Carter, G. E.; Harris, H. C. *J. Chem. Soc., Chem. Commun.* **1984**, 388.

(20) Batts, B. D.; Gold, V. *J. Chem. Soc. A* **1969**, 984, Fife, T. H.; McMahon, D. M. *J. Am. Chem. Soc.* **1969**, *91*, 7481; *J. Org. Chem.* **1970**, *35*, 3699, Menger, F. M.; Venkatasubban, K. S. *Ibid.* **1976**, *41*, 1868.

(21) Dorshow, R. B.; Bunton, C. A.; Nicoli, D. F. *J. Phys. Chem.* **1983**, *87*, 1409.

micelles have been observed in hydrolyses of benzoyl chlorides, alkyl halides, and sulfonic esters, but with the glycine derivative (B1-12) nuclephilic participation by the carboxylate moiety is important.

Zwitterionic micelles of the glycinate-derived surfactant (B1-12) have a carboxylate moiety which can attack the sulfonyl group. As for reactions of the nonmicellized betaine (Table I) kinetics are clearly first order so there is no indication of buildup of a mixed anhydride under the reaction conditions. The overall micellar effects depend upon the balance between inhibition of the spontaneous reaction and rate enhancement due to nucleophilic participation by the carboxylate moiety, although nucleophilic attack predominates. The various reactions are shown in Scheme III.

It is difficult to separate the contributions of the various reactions except for the 4-bromo and 4-nitro derivatives (**1d** and **1e**). With these compounds nucleophilic attack by the carboxylate moiety in the micelle is so much faster than the other reactions that we can neglect their contributions and the first-order rate constant is given by[22]

$$k_\psi = m_N{}^s k_M K_S([D] - \mathrm{cmc})/(1 + K_S([D] - \mathrm{cmc})) \quad (3)$$

where $k_M$ is the second-order rate constant of reaction in the micelle, expressed in terms of the mole ratio $m_N{}^s$ of carboxylate moiety to total surfactant.[23]

The values of $k_M$ are 0.028 and $\approx 0.3$ $s^{-1}$ for the bromo and nitro derivative, respectively (eq 3 and Table IV). Second-order rate constants in micelles can be compared with those in water, or other solvents, provided that both are expressed in the same units. The rate constants in the micelle, $k_M$ (eq 3) are expressed in reciprocal seconds, because mole ratios are dimensionless. They can be converted into second-order rate constants, $k_2{}^m$, $M^{-1}$ $s^{-1}$, by writing concentration as molarity in the micellar pseudophase. The conversion factor is the molar volume of the reaction region, which has been assumed to be 0.14 L, based on the volume of the Stern layer of a nonfunctional micelle.[24,25] This value will be used here, eq 4, although it may be too low for a functional micelle such as that of the betaine surfactant (B1-12).

$$k_2{}^m = 0.14 k_M \quad (4)$$

The values of $k_2{}^m$ are 0.004 and 0.04 $M^{-1}$ $s^{-1}$ for the bromo and nitro derivatives, respectively. These values can in principle be compared with those of the second-order rate constants, $k_W$, $M^{-1}$ $s^{-1}$, for reaction of **1d,e** in water which are approximately 0.006 and 0.015 $M^{-1}$ $s^{-1}$ for the bromo and nitro derivatives, respectively (Table I). The values of $k_W$ are only approximate because we neglect medium effects of the betaine, but despite these uncertainties the second-order rate constants in the micelles of B1-12 are similar to those in water. This similarity has been observed for reactions in other functional micelles and comicelles[22,26b,27] and is consistent with the generalization that rate enhancements of most bimolecular reactions are due largely to concentration of the two reactants in the micellar pseudophase.[14,24,26-29]

Electron-withdrawing groups, e.g., $NO_2$ or Br, increase the importance of bond-making as compared with bond-breaking and their role is evident from the rapid reactions in cationic micelles of CTACl or zwitterionic micelles of SB3-16 (Tables II, III, and V). Similar micellar effects have been observed in reactions of aryl chloroformates and benzoyl chlorides.[5,6]

## Experimental Section

**Materials.** The surfactants were prepared or purified by standard methods, except for the sulfobetaine (SB3-16) which was provided by Dr. K. Jones of Unilever Research. The arenesulfonyl chlorides were commercial samples and were distilled or recrystallized. Solutions were made up in deionized, redistilled $H_2O$.

**Kinetics.** Reactions were followed spectrophotometrically with Hewlett-Packard diode-array or Gilford spectrophotometers at 25.0 °C in water. The wavelengths were 230 nm for benzenesulfonyl chloride and 270, 245, 250, and 282 nm for the 4-methoxy, 4-methyl, 4-bromo, and 4-nitro derivatives, respectively. Reaction with $OH^-$ was suppressed by addition of $10^{-3}$ M HCl. All reactions followed first-order kinetics for at least 4 half-lives. [Substrate] was $10^{-5}$ M, and reaction was started by adding substrate in 2–6 $\mu$L of MeCN to 1–3 mL of the aqueous solution, so that the solution contains 0.1% MeCN.

The sulfobetaine surfactant (SB3-16) is not sufficiently soluble to be used at high concentration, and we took care to avoid precipitation in the course of reaction.

**Acknowledgment.** Support of this work by the Army Office of Research is gratefully acknowledged.

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[22] Bunton, C. A.; Hamed, F. H.; Romsted, L. S. *J. Phys. Chem.* **1982**, *86*, 2103.

[23] This mole ratio equals 1 under our conditions.

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

[25] Other estimates of this value range up to 0.35 L,[26] and its value probably depends upon the particular reaction and surfactant.

[26] (a) Cuccovia, I. M.; Schröter, E. H.; Monteiro, P. M. Chaimovich, H. *J. Org. Chem.* **1978**, *43*, 2248. (b) Fornasier, R.; Tonellato, U. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1301.

[27] Bunton, C. A. *Catal. Rev. Sci. Eng.* **1979**, *20*, 1.

[28] Martinek, K.; Yatsimirski, A. K.; Levashov, A. V.; Berezin, I. V. In "Micellization, Solubilization and Microemulsions", Mittal, K. L., Ed.; Plenum Press: New York, 1977; Vol. II, p 489.

[29] Micelles can exert a medium effect on bimolecular, nonsolvolytic reactions, especially of nonionic nucleophiles, and unimolecular reactions which is generally understandable in terms of the polarity of the micellar surface.[10,24,27,28]