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REAGENT DISTRIBUTION AND MICELLAR CATALYSIS OF 4-SUBSTITUTED BENZENESULFONYL CHLORIDE REACTIONS

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Reactions of OH^- and HCO_2^- with 4-nitro, 4-bromo, and 4-methylbenzenesulfonyl chloride derivatives have been examined in solutions of cetyltrimethylammonium chloride, hydroxide and formate. Rate effects were analyzed quantitatively in terms of distribution of reactant between water and micellar pseudophases. Second-order rate constants at the micellar surface are very similar to that in water for reactions with HCO_2Na while for reactions with OH^- the second-order rate constants at the micellar surface is considerably smaller than that in water.

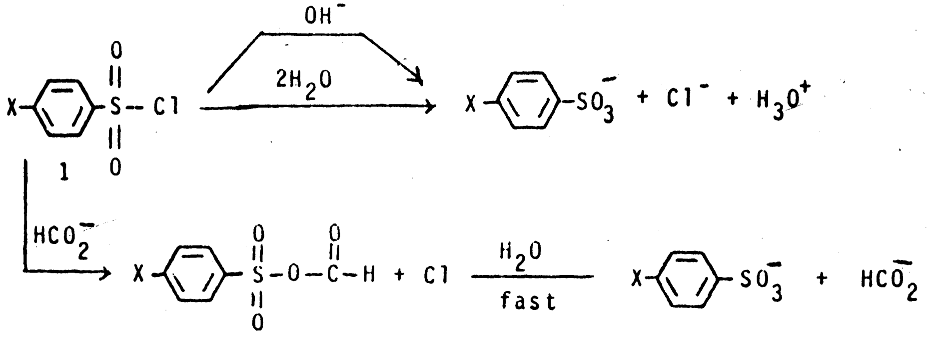
INTRODUCTION

The nucleophilic reaction with a sulfur atom of a sulfonyl derivative or a sulfonante ester has been discussed in terms of either a Synchronous S_N2-type or an addition- elimination mechanism.[1–5] For nonsolvolytic reactions there is important depndenc on both the ease of departure of the leaving group and the reactivity of the reacting nucleophile. All the evidence suggest that solvent molecules participate as nucleophiles in hydrolysis of sulfonyl chloride,[5] for example, but there is no evidence for an S_N1-like ionization.[3,5] Most reactions have been examined in aqueous organic mixtures or organic solvents.

Cationic and anionic micelles generally inhibit spontaneous hydrolysis of carboxylic anhydrides,[6,7,9,10] carbonate esters,[6,7,8,10] acyl chlorides,[6,7,9] alkyl halides,[6,7,9,10] perbenzoate,[11] and sulfonate esters.[6,12,13] The inhibition is understood, because all these reactions are inhibited by a decrease in the water content of a mixed solvent[14,15] and micellar surfaces appear to be less polar than that of a bulk water.[10,16] In addition ionic micelles appear to have charge effects,[5,6,9,12] not only that but micellar bound water may be less reactive than bulk water, although evidence is conflicting on this matter.[6,17–19] Reaction which have an S_N1 like character such as alkyl halides are faster in nonionic than in cationic micelles, although they are slower than in water. Hydrolysis of carboxylic anhydride or carbonate ester are faster in cationic than in anionic micelles.

This test has been applied to hydrolysis of substituted benzoyl chloride,[6,7,10] aryl chloroformates[6,7,10] and 4-substituted benzenesulfonyl chloride[5]. 4-Substituted benzenesulfonyl chlorides are convenient substrates for study of micellar effects upon reaction rate because the reaction mechanism are well understood[1-5,13] and the reaction can be followed easily in dilute surfactant. We examined micellar effects upon reactions of substituted benzenesulfonyl chloride (la-c) with OH^- and formate ions in water (Scheme I).

SCHEME I



1a $X = NO_2$ **1b** $X = Br$ **1c** $X = CH_3$

The reagents were chosen so that the first step is followed kinetically. For example, in the reaction of toluenesulfonyl chloride with carboxylate ion we used formate ion, because the first formed mixed anhydride goes readily to products,[5,7] and carboxylate ions are general-base catalysts of water reaction.[20]

Reactions were carried out in aqueous solution of cetyltrimethylammonium surfactant (CTAX, n- $C_{16}H_{33}\overset{+}{N}MeX^-$) where X^- = Br^-, Cl^-, OH^-, or RCO_2^-). Typically the rate-surfactant profile, of bimolecular reactions go through maxima with increasing [surfactant] with constant [nucleophile] and an inert surfactant counterion.[10,21,22] In deacylation by OH^- in CTABr the rate maxima can be ascribed to the combination of competition between OH^- and Br^- for the micelle and distribution of the substrate between water and micelles.

However if only reactive counterions are in solution, the rate constants should become constant once all the substrate is micellar bound, provided that the micelle is saturated with counterions. This predicated behaviour is observed for reactions in micellized alkanesulfonic acid[23], and in micellized CTACN[24]. Nucleophilic reactions in CTAOH and CTAF do not fit this pattern[7,23-27], and it appears that here the concentration of micellar bound OH^- or F^- increases with increasing total concentration. We were interested, therefore, in studying nucleophilic attack upon heteroatoms in micellized creative ion surfactants where the nucleophile or base was OH^- or RCO_2^- and in CTABr, CTACl with added inert counterions.

EXPERIMENTAL

Materials

The arenesulfonyl chloride were commercial samples and were distilled or recrystallized. The surfactants were prepared or purified by standard methods[23]. The other surfactant such as cetyltrimethylammonium formate was prepared in solution from CTAOH[7] by neutralization with equimolar formic acid. The preparation and manipulation of CTAOH was done under N_2 in the absence of CO_2. The surfactant concentration was calculated from that of CTAOH. Solutions were made up in deionized, redistilled H_2O.

Kinetics

The reactions were followed spectrophotometrically at 25°C in water. The wave lengths were 251, 249 and 245 nm for the 4-nitro, 4-bromo and 4-methyl derivatives, respectively. The reaction with OH^- generated by autoprotolysis was suppressed by addition of 10^{-3}M HCl or carboxylic acid. All reactions followed first-order kinetics for at least 4 half-lives and the first-order rate constants, k_ψ, are in reciprocal seconds. Substrate concentration was 10^{-5}M, and reaction was started by adding substrate in 3–7 u of MeCN to 1–3 ml of the aqueous solutions so that the solution contains 0.1% MeCN.

Reactions in the absence of surfactant were followed by using dilute nucleophile or base (< 0.04 M) to minimize kinetic salt effects. The spontaneous water catalyzed reactions make minor contribution[5], except in the reaction with OH^- and we correct for them in analyzing the rate data in the absence of surfactant.

RESULTS AND DISCUSSION

Reactions in the Absence of Surfactant

The second-order rate constants (k_W) for reactions with OH^- at 25°C are 100, 60 and 21 $M^{-1}s^{-1}$ for *p*-nitrobenzenesulfonyl chloride, *p*-bromo and *p*-methyl derivatives, respectively, and for reactions with format ion $k_W = 0.20$, 0.064 and 0.051 $M^{-1}s^{-1}$ for *p*-nitro, *p*-bromo and *p*-methyl derivatives respectively. Reactions of benzenesulfonyl chloride in water is speeded by formate ion (Table 2) and the reactions occur by nucleophilic attack, giving a mixed anhydride, which in our system should be short lived.[5,29] (The common carboxylate ion is a general base catalyst, but this reaction is relatively slow).

Reactions in the Presence of CTACl

The reactions of substrates (la-c) with OH^- or HCO_2^- are speeded by micellized CTACl (Figures 1 and 2). As generally found, k_ψ goes through maxima with increasing [CTACl] and constant [anion], and added Cl^- inhibits reaction by competing with the reactive anion for the micelle,[7,10,21] (Table 1).

TABLE 1
INHIBITION BY CHLORIDE ION OF REACTIONS OF 4-SUBSTITUTED BENZENESULFONYL CHLORIDE (Ia-c) WITH HCO_2Na IN CTACl[a]

10^4 [CTACl] *M*	k_ψ^b		
	Ia	Ib	Ic
3	0.042	0.032	0.014
6	0.092	0.051	0.019
10	0.098	0.071	0.021
40	0.31 (0.28)	0.13 (0.11)	0.033 (0.031)
70	0.44 (0.42)	0.15 (0.14)	0.040 (0.041)
100	0.50 (0.48)	0.16 (0.16)	0.042 (0.042)
300	0.56 (0.55)	0.16 (0.17)	0.038 (0.039)
600	0.51 (0.52)	0.14 (0.15)	0.034 (0.036)
1000	0.48 (0.48)	0.11 (0.13)	0.028 (0.030)
1500	0.43 (0.45)	0.09 (0.10)	0.021 (0.022)

[a] values of k_ψ in reciprocal seconds at 25°C. Predicted values are in parenthesis.
[b] in 0.05 *M* HCO_2Na and 0.05 M NaCl.

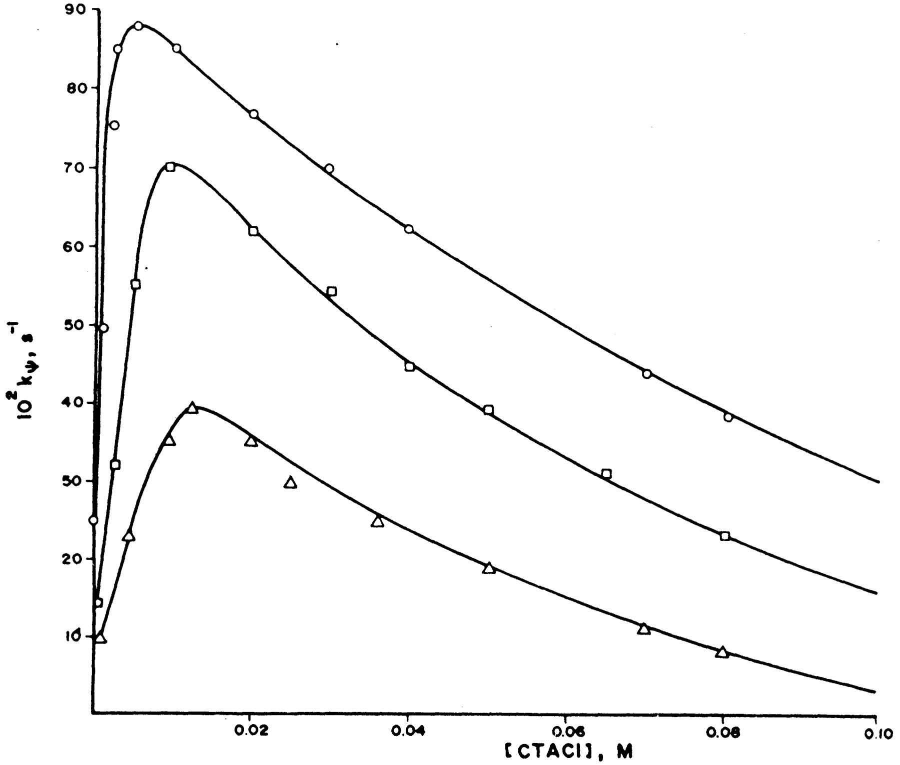


Fig. 1. Reactions of substituted benzenesulfonyl chloride with NaOH in CTACl (O) 5×10^{-4}*M* NaOH with Ia, (□) 8×10^{-4} M NaOH with Ib, (Δ) 10^{-3} M NaOH with Ic.

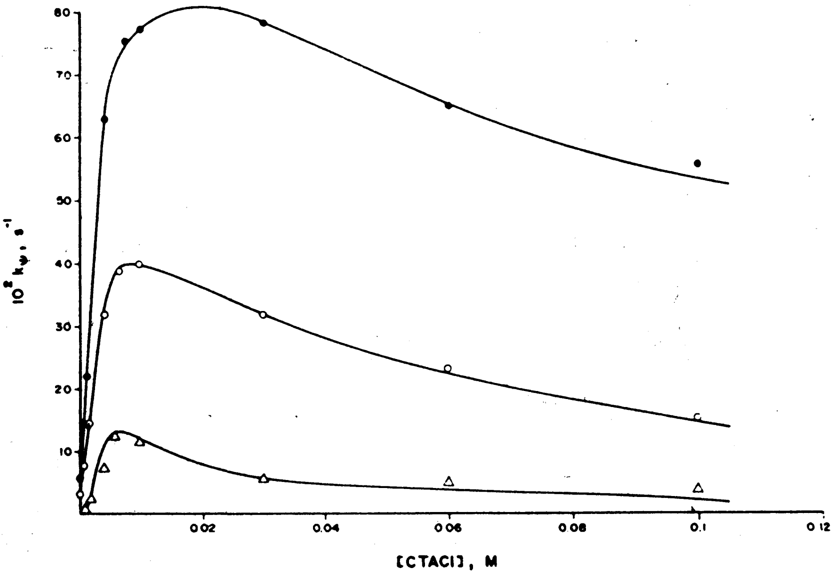


Fig. 2. Reactions of substituted benzenesulfonyl chloride (Ia-c) with HCO_2Na in CTACl, (●) 0.03 M HCO_2Na with Ia, (O) 0.05 M HCO_2Na with Ib, (Δ) 0.05 M HCO_2Na with Ic.

TABLE 2
EFFECTS OF FORMATE ION ON THE HYDROLYSIS OF 4-SUBSTITUTED BENZENESULFONYL CHLORIDE (Ia-c)[a]

[HCO_2Na] M	$10^3 k_\psi$		
	Ia	Ib	Ic
0.03	8.97	4.20	5.29
0.05	12.90	5.46	6.03
0.07	16.7	6.74	7.43
0.1	21.90	7.93	8.71
0.13	28.1	10.29	10.10
0.16	34.50	12.41	11.65
0.2	40.9	14.54	12.81

[a]values of k_ψ in reciprocal seocnds at 25°C. The first-order rate constants, 10^3 k_ψ, s^{-1} for spontaneous hydrolysis of substrate (Ia-c) in water are as follows: 4-Nitro, 2.7; 4-Bromo, 2.1; 4-Methyl, 3.4.

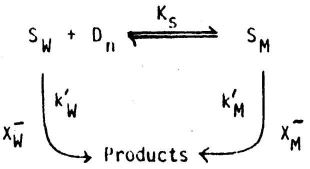
Reactions in Reactive Ion Micelles

The first-order rate constants increase smoothly with increasing [CTAOH] or [CTAFor]. Added nucleophile increases, k_ψ, but only to a small extent at higher [surfactant], and at higher surfactant or nucleophile concentration k_ψ tends toward limiting values (Figures 3 and 4). Observation of rate enhancement in the micelle as compared with that in water is understandable because the concentration of hydroxide or carboxylate ion at the micellar surface will be greater than in the aqueous pseudophase[21].

Reactions in the Presence of Reactive Counterion Surfactant

We assumed that the distribution of substrate between aqueous and micellar pseudophase follows Scheme II[30]. In Scheme II, S denotes substrate and D_n the micellized surfactant.

SCHEME II



There is also a reaction with water, which make a (minor) contribution, k_{H_2O}, to the observed rate constant[5]. With our substrates(la-c) nucleophilic attack by the carboxylate moiety or OH^- in the micelle is so faster then the other reactions that we can neglect their contributions[5] and the first-order rate constant is given by.[10,30]

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

where K_s is the binding constant of substrate to micelles, written in terms of the concentration of micellized surfactant, and k'_W and k'_M are respectively the first-order rate constants in the aqueous and micellar pseudophases. The rate constants can be written in terms of the second-order rate constants, k_W and k_M and the concentration of OH^- or carboxylate ion in each pseudophase, Eq. 2 and 3.

$$k'_W = k_W[X_W^-] \tag{2}$$

$$k'_M = k_M m_x^s = k_M[X_M^-]/[D_n] = k_M\beta \tag{3}$$

Equations 1–3 give Eq. 4, 5 and 6.

$$k_\psi = \frac{k_W[X_W^-] + k_M K_s m_x^s[D_n]}{1 + K_s[D_n]} \tag{4}$$

$$= \frac{k_W[X_W^-] + k_M K_s[X_M^-]}{1 + K_s[D_n]} \tag{5}$$

$$= \frac{k_W(X_T^-) - [X_M^-] + k_M K_s[X_M^-]}{1 + K_s[D_n]} \tag{6}$$

For a reactive ion surfactant the molar ratio, m_x^5 of bound ion to micellar head groups is given by β,[10,23–26] the fractional extent of charge neutralization of the head

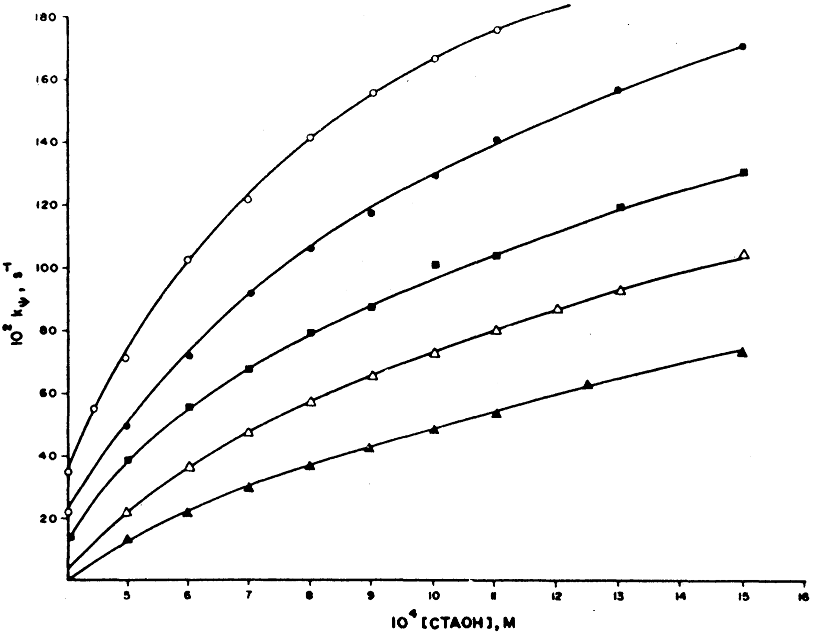


Fig. 3. Reactions of substituted benzenesulfonyl chloride (Ia-c) in CTAOH. ●, ■, ▲, in CTAOH alone with substrates (Ia-c) respectively. O, Δ, in CTAOH + $3\times10^{-4} M$ NaOH with substrate Ia and Ic respectively.

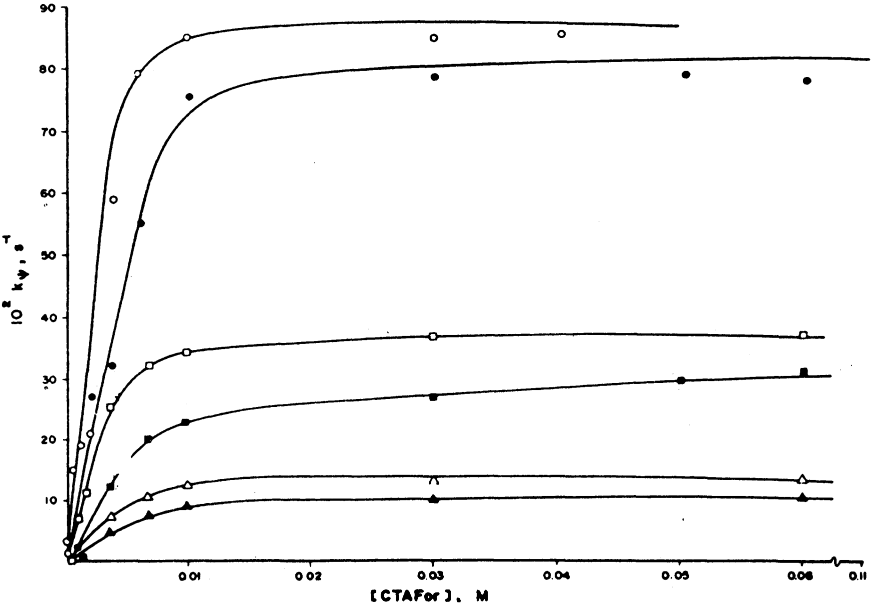


Fig. 4. Reactions of substituted benzenesulfonyl chloride (Ia-c) in CTAFor, ●, ■, ▲ in CTAFor alone for (Ia-c) respectively. O, ☐, Δ in CTAFor + 0.02 M HCO2Na For (Ia-c) respectively.

For a reactive ion surfactant the molar ratio, m_x^s of bound ion to micellar head groups is given by β,[10,23-26] the fractional extent of charge neutralization of the head groups. Therefore, if β is independent of the concentration of the surfactant or added reactive ion, X^-,[11,21,31] Eq. 7 holds

$$k_\psi = k_M\beta \qquad (7)$$

Once the substrate is fully micellar bound and K_ψ should then reach a constant value. This behaviour has been observed for reactions involving hydrogen ions,[23] for nucleophilic addition by CN[24], and for substitutions by Br^-[32]. However, for reactions of very hydrophilic anions, e.g., OH^- or F^-, values of k_ψ increases with increasing concentration of nucleophile or surfactant, even when the substrate is fully micellar bound[21,23,24]. We see this apparently anomalous behaviour for reactions of benzenesulfonyl chloride derivatives with OH or RCO_2 (Figures 3 and 4). Therefore, for a number of reactions the rate-surfactant profiles cannot be explained in terms of the simple model which assumes constancy of β. But they can be fitted to a model which assumes that the apparent value of β increases with increasing concentration of the reactive counterion[27].

The distribution of the reactive counterion, X^-, between the aqueous and micellar pseudophases is written in terms of Eq. 8, which is akin to the Langmuir isotherm,

$$K'_x = [X^-_M]/[X^-_W]([D_n] - [X^-_M]) \qquad (8)$$

where K'_x can be regarded as a binding constant assumed to be independent of the charge neutralization of the micelle.

Added electrolyte can contribute to $[X^-]$, and $[X^-_T]$ is the total amount of X^-, regardless of its origin. Equation 8, as written, assumes that micellar charge varies with concentrations of surfactant and counterion, and we use it empirically in treating the kinetic data. Combining Eq. 6 and 8 and the mass balance give.[27,32]

$$k'_x[X^-_M]^2 - (K'_x[D_n] + K'_x[X^-_T] + 1)[X^-_M] + K'_x[D_n][X^-_T] = 0 \qquad (9)$$

(for solutions of only CTAOH or CTAFor $[X^-_T]$ is the total concentration of surfactant *[D]*)

Equation 9 can be used to calculate the $[X^-_M]$ and $[X^-_W]$ as a function of D_n and $[X^-_T]$ for various assumed values of the ionic binding constant K'_x. We include the concentration of X^-_W to allow for a contribution of reaction in the aqueous pseudophase, using known values of k_W,[23,27,29] but neglect of it has little effect on the predicted rate-surfactant profile for our reactions.

Our approach is to use Eqs. 4, 8 and 9 to stimulate the variation of k_ψ (Eq. 5) with concentration of surfactant or added nucleophile. The second-order rate constants, k_W, are measured directly and k_M, K_s and K'_x are treated as adjustable parameters. However, for dephosphorylation and aromatic nucleophilic substitution and ester hydrolis in CTAOH $K'_{OH} = 55\ M^{-1}$,[7,10,27] and we use this value here. The critical micelle concentration, cmc, is also treated as an adjustable parameter, although its value in kinetic system is assumed to be similar to that of CTAOH or similar C_{16} surfactant in water. We take K_s = 150 M^{-1} for substituted benzenesulfonyl chloride. The cmc was taken to be $5 \times 10^{-4} M$ for CTAOH and 8×10^{-4} for the corresponding formate. Changes in these values had no effect except in very dilute surfactant.

The variations of k_ψ for reactions of the substrates (la-c) is solutions of CTAOH and related formate surfactants CTAFor, can be simulated by using this treatment and the fit is illustrated in Figures 3 and 4, where the solid lines are calculated. The treatment can also be applied to experiments with added OH^- or formate ion; (in fitting the data we include formally a term for reactions in the aqueous pseudophase, but its contribution to the overall rate constant is negligible). The ion binding parameters were $K'_{OH} = 55 M^{-1}$ under all conditions, $K_{For} = 75–85 M^{-1}$ (the values are footnoted in Table 3). Our estimate of k_M are given in Table 3.

TABLE 3

VALUES OF K_M^a

Reaction	conditions[b]			
	1	2	3	4
p – $O_2NC_6H_4SO_2Cl + OH^-$	2.10	2.2	1.80	1.90
p – $NO_2–C_6H_4SO_2Cl + HCO_2^-$	1.0[c]	1.1[c]	1.0	0.90
p – Br – $C_6H_4SO_2Cl + OH^-$	1.62	—	1.40	
p – Br – $C_6H_4SO_2Cl + HCO_2^-$	0.40	0.43	0.5	0.45
p – Me – $C_6H_4SO_2Cl + OH^-$	0.90	1.1	0.8	
p – Me – $C_6H_4SO_2Cl + HCO_2^-$	0.15	0.18	0.19	0.16

[a] values of k_M in reciprocal seconds at 25°C.

[b] 1. reactive counterion surfactant; 2. reactive counterion surfactant plus counterion; 3. CTACl; 4. CTACl + Cl^-. [c] $K_{For} = 85 M^{-1}$ in the other experiments a value of $70 M^{-1}$ was used.

Reactions in CTACl

The variations of k_ψ with [CTACl] follows the generally accepted treatment of rate enhancement of bimolecular reactions by micelles.[10,21,26] In fitting our data in CTACl we assumed that X^- reactive anion X^- and inert anion Cl^- complete for the micelle according to equation 10[10,21]. The fraction of head groups neutralised

$$K_{Cl}^{x} = [Cl_M^-][X_W^-]/[Cl_W^-][X_M^-] \qquad (10)$$

by counterions β is given by 1 - α, where α is the fractional ionization of the micelle. Equation 10 with the mass balance condition, gives m_x^s in terms of various parameters characteristic of the micelle (equation 11).[21,37]

$$(m_x^s)^2 + m_x^s\left(\frac{[X_T^-] + K_{Cl}^{x}[Cl_T^-]}{(K_{Cl}^{x} - 1)[D_n]} - \beta\right) - \frac{[X_T^-]\beta}{(K_{Cl}^{x} - 1)[D_n]} = 0 \qquad (11)$$

Equations 1–3 and equations 10 and 11 can be combined, allowing simulation of rate-surfactant profiles using a simple computer program[37,40]. Assumptions and approximations in this treatment have been discussed.[21,37,40] In particular, for pseudophase model may fail at high ionic concentrations[41] and there are questions as to values of k_x^{OH} and β[19,37,42]. In our calculation we took β = 0.8[21,31], values of $K_{Cl}^{x} = 5\ M^{-1}$ for all the added anions. We assumed that values of K_s, are similar to those which fit the data for reactions in reactive counterion micelles (Figures 3 and 4), i.e. 150 M^{-1}, for all derivatives of benzenesulfonyl chloride (la-c).

The cmc of CTACl was assumed to be lowered by added electrolyte to 4×10^{-4}M in NaOH and 6×10^{-4} in HCO_2Na. Variations in cmc or K_s had no effect on the predicted rate-surfactant profiles except in very dilute surfactant. The "best fit"s values of k_M for reactions in CTACl and in the reactive counterion surfactants are given in Table 3.

The values of $K_{Cl}^{OH} = 5$ is similar to those determined in other kinetic or equilibrium systems[11,25,35-37,43]. The corresponding ion-exchange parameter for formate ion in CTACl is similar to K_{Cl}^{OH} suggesting that formate ion is not hydrophobic enough to interact strongly with the micelle.[36]

Comparison of Reactions in CTACl and Reactive Counterion Surfactants

The simple distribution models fit the kinetic data reasonably well for reactions in CTAOH, CTAFor and CTACl with the parameters given in Table 3 as shown by the agreement between the experimental data and the computer plots in Figures 1–4. Eventhough the treatment of the reactions in reactions in reactive surfactant (Eq. 4, 8 and 9) and those in CTACl (Eqs. 1–3, 10 and 11) appear to be based on completely different premises and use different approximates, but, nontheless, they lead to similar values of such parameters as k_M and K_s. The treatment of the reactions in CTACl based on the ion-exchange model which typically dependent on the assumption that β is constant which appears to fail when only reactive counterion surfactant with hydrophilic anion that have high charge density, e.g. OH^- or F,$^-$[21,23,24] but when the counterion is the more hydrophobic such as CN^- or Br^-[24,32] the treatment is satisfactory.

The analysis of the reactions is CTAOH and CTAFor based on the application of the mass action model which predicts that β will vary with [counterion].

Using Eq. 8 allowed us to treat the variable extents of binding of reactive hydrophilic counterion to a micelle and leads to a reasonable fit between observed and predicted rate surfactant profiles (Figures 3 and 4), i.e. it is describing the distribution of counterions between aqueous and micellar pseudophases. However, this distribution may be governed by a wide distribution of micellar sizes ranging from relatively small micelles which bind the counterion weakly to normal sized micelles which bind it more strongly[27,32]. We conclude that both treatment appear to have its own limited range of applicability.

Comparison of Reactions in Micellar and Aqueous Pseudophase

The second-order rate constants, k_M of reactions in the micellar pseudophase have the dimensions of reciprocal time, because the concentration of X^- is written as a mole ratio. This choice of units allows an unambigous definition of concentration in the micellar pseudophase, but k_M cannot be compared directly with the second-order rate constants in water, k_W, whose units are generally $M^{-1}s^{-1}$. But comparison can be made provided that we specify the volume element of reaction in the micellar pseudophase, which could be that of the micelle or of its Stern-layer. Elsewhere the molar volume of the Stern-layer of CTACl or CTABr has been assumed to be 0.14*L*,[7,13,37] and we denote this value as V_M so that

$$k_2^m = k_M V_M \tag{12}$$

where k_2^m, $M^{-1}\ s^{-1}$, can be compared directly with k_W. The various rate constants are compared in Table 4 by taking averages of the values in Table 3

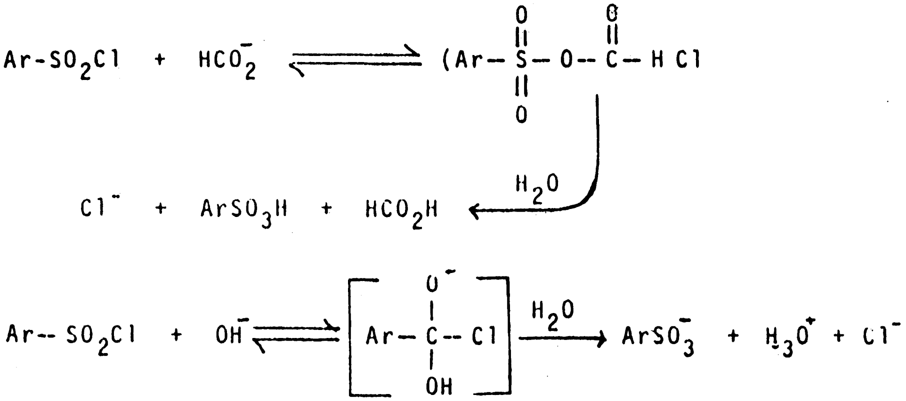
For reactions of benzenesulfonyl chloride derivatives (Ia-c) with HCO_2Na values of the second-order rate constants k_W and k_2^m in the aqueous and micellar pseudophases are similar as is often found for reactions of nucleophilic anions.[10,24,32,37]

The second-order rate constants for reactions of substrates(Ia-c) with hydroxide ion are considerably smaller in micelles than in water, (Table 4). These differences between reactions of (Ia-c) with OH^- and with HCO_2^- could be due to mechanism. Reaction of substrates(Ia-c) and formate ion goes via s mixed anhydride,[29] which should react rapidly with water. In reaction with OH^- in a micelle reaction could involve formation of an intermediate which either returns to reactant or goes forward to products; alternatively, addition of OH^- could be concerned with loss of chloride ion. The concerned mechanism seems more realistic (Scheme III) and we should point 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 accomodate negative charge,[1,4] especially with strong nucleophile[5].

TABLE 4
REACTIONS IN WATER AND IN MICELLES

Reaction	$k_M\ s^{-1}$	$k_2^m\ M^{-1}\ s^{-1}$	k_2^m/k_W
$p-O_2N-C_6H_4SO_2Cl + OH^-$	2.0	0.28	0.0028
$p-O_2N-C_6H_4SO_2Cl + HCO_2^-$	1.0	0.14	0.70
$p-Br-C_6H_4SO_2Cl + OH^-$	1.5	0.21	0.0035
$p-Br-C_6H_4SO_2Cl + HCO_2^-$	0.50	0.07	1.1
$p-Me-C_6H_4SO_2Cl + OH^-$	0.90	0.13	0.0062
$p-Me-C_6H_4SO_2Cl + HCO_2^-$	0.17	0.021	0.47

SCHEME III



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