may also be caused by chemical reactions of the metal or the semiconductor. Examples are the uptake of hydrogen by platinum or titanium dioxide, which changes the work function or the Fermi level, respectively. Another example is the formation of new surface states at the surface of the semiconductor, which have energy levels appropriate for an efficient transfer of electrons from the semiconductor to the metal. The third possibility is a quantization effect due to the small particle dimensions (TiO_2 , 100 nm; Pt, 5 nm). For example, the number of charge carriers in the metal can be of the same order of magnitude or even less than the number in the space charge layer of the semiconductor, which violates the basic assumption of an indefinite reservoir of charge carriers in the metal. The statistics and distribution of charge carriers and consequently the internal field distribution would drastically change under this condition. Our experimental results confirm the assumption based on photocatalytic experiments mentioned above²⁴ that excess electrons move to the platinum islands, where the subsequent reduction of a substrate such as protons takes place.

3.5. Platinized Titanium Dioxide with 2-Propanol. The photocatalytic hydrogen evolution in platinized titanium dioxide can be enhanced by the addition of hole scavengers as in untreated titanium dioxide. Figure 3 (curve b) shows the transient photoconductivity of platinized titanium dioxide after the addition of 2-propanol. Also, at excitation densities higher than displayed in Figure 3 the decay observed is slower similar to platinized TiO₂ without 2-propanol, which is probably due to the same saturation process. At lower excitation densities the decay observed is identical with that of curve b in Figure 3 characterized by a power law with an exponent of about -0.25, which means that the decay is slower than without 2-propanol (exponent of about -0.35, curve c in Figure 3), but not as slow as in the case of unplatinized powder treated with 2-propanol (curve a in Figure 2). This suggests that a part of the decay in the platinized sample is caused by a process identical with that in the unplatinized samples. This process may be ascribed to an electron-hole recombination at the surface of the TiO₂ particles via surface states. The electron decay channel induced by platinization is probably due to the transfer of excess electrons from the titanium dioxide to the platinum.

4. Summary

The present work shows that useful information on excess charge carrier kinetics in semiconductor powders can be obtained with transient photoconductivity measurements. It is observed

(32) Memming, R. Fundamentals and Developments of Photocatalytic and Photoelectrochemical Processes; Schiavello, M., Ed.; NATO ASI Series, Series C, 146; Reidel: Dordrecht, 1985; p 107. in TiO_2 powder that the excess electron decay takes place over an extended time range. This indicates a braod distribution in energy of states that immobilize excess electrons, but this does not adequately explain the present experimental data, in which the decay in untreated P25 powder is characterized by a power law and does not depend on the excitation density over a relatively large range. It is plausible that thermal emission from a broad distribution of states is involved in the immobilization of electrons in TiO_2 powder. In the untreated powder there is a recombination of the excess charge carriers, which extends over several orders of magnitude in time. Most probably the recombination proceeds via a trapping of the excess holes at the surface under the formation of hydroxyl radicals (OH[•]) followed by a reaction of electrons with these species. The broad energetic distribution of these species may explain the extended time range of the electron decay observed (Figure 1), where thermal activation may also play a role. However, electrostatic interactions (e.g., space charge) may play a role as well.

After the addition of a hole scavenger, i.e., 2-propanol, the electron decay rate decreases, which is explained by preferential trapping of holes in states with a low recombination rate due to the presence of 2-propanol. This does not exclude that in the powder treated with 2-propanol the excess holes are also trapped at the surface under formation of hydroxyl radicals (OH $^{\circ}$). However, in contrast to the untreated powder, these radicals are only intermediates before the hole is transferred to the hole scavenger. This points to an enhanced charge-carrier separation in P25 powder under the influence of 2-propanol.

The results of tetranitromethane addition can be explained as the counterpart of that of 2-propanol, i.e., fast electron trapping in states induced by tetranitromethane.

A better separation of electrons and holes can be achieved by the platinization of the titanium dioxide. It is likely that holes behave as in untreated TiO_2 and they form oxidizing oxygen species at the surface. On the other hand, some of the electrons interact with states induced by platinum and are separated spatially and/or energetically from the holes. The enhanced charge-carrier separation and the catalytic effect of platinum enhance the efficiency of the photocatalytic hydrogen evolution in platinized TiO_2 .

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Registry No. TiO₂, 13463-67-7; Pt, 7440-06-4; C(NO₂)₄, 509-14-8; ratile, 1317-80-2; anatase, 1317-70-0; 2-propanol, 67-63-0.

Micellar Effects upon the Rates of S_N2 Reactions of Halide Ions

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Observed first-order rate constants for reactions of Cl^- or Br^- with substituted alkyl benzenesulfonate (1a-c) in micelles of cetyltrimethylammonium surfactants (CTAX, X = Cl, Br, OMes, 0.5SO₄) increase monotonically with increasing [CTACl] or [CTABr] or halide ion concentration and tend to limiting values. In CTAOMes or (CTA)₂SO₄, the rate constants go through maxima. The variation of the rate constants with concentrations of surfactant and halide ion can be fitted to an equation that accounts for the distribution of both reactants between water and micelles, i.e., in terms of ion-exchange and mass-action models. The second-order rate constants in the aqueous and micellar pseudophases are similar.

Aqueous micelles speed bimolecular reactions by bringing reactants together or inhibit them by keeping reactants apart.^{1-4,13}

The enhancements can be treated quantitatively by estimating reactant concentration at the micellar surface.⁴ It is usually easy



to measure directly the concentration of a nonionic reactant in the micellar pseudophase,¹⁻⁷ but it is often more difficult to do this with ionic reagents. An indirect approach to this problem is to assume that counterions compete for ionic sites on the micellar surface and this distribution is governed by an ion-exchange equilibrium,³⁻⁷ and that the fraction of counterions that neutralize these sites, β , is approximately constant.³⁻⁷ This approach explains, quantitatively, micellar effects upon a number of reaction rates and equilibria and leads to equations which describe the competition between counterions for an ionic micelle.^{6,8,10}

Ion exchange is described by eq 1 for micellar binding of a nucleophile, X⁻, to a cationic micelle having Y⁻ as an inert counterion, where the subscripts M and W denote the micellar and aqueous pseudophases, respectively. The ion-exchange constant K_X^{\diamond} is given by eq 2.

$$X_{M}^{-} + Y_{W}^{-} \rightleftharpoons X_{W}^{-} + Y_{M}^{-}$$
(1)

$$K_{\rm Y}^{\rm X} = [{\rm X}_{\rm W}^{-}][{\rm Y}_{\rm M}^{-}]/[{\rm X}_{\rm M}^{-}][{\rm Y}_{\rm W}^{-}]$$
(2)

Typically, the observed rate constants of bimolecular reactions go through maxima with increasing [surfactant] at constant [nucleophile] and inert surfactant counterion.⁵⁻¹² In alkyl benzenesulfonate dealkylation by Cl⁻ or Br⁻ in (CTA)₂SO₄ or CTAOMes, the rate maxima can be ascribed to the combination of competition between Cl⁻ or Br⁻ and SO₄²⁻ or OMes for the micelle and substrate distribution between micelles and water.

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 predicted behavior is observed for reaction involving hydrogen ions,¹³ for nucleophilic addition of $CN^{-,14}$ and substitution by $Br^{-,10,17,18}$ However, for reactions of very hydrophilic anions, e.g., OH^- , HCO_2^- , or F^- , values of k_{ψ} increase with [surfactant], even when the substrate is fully micellar bound.¹⁵⁻¹⁹

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TABLE I: Reactions in the Absence of Surfactant^a

	substrate ^b				
[salt], M	1a	1b	1c		
0.08	3.5 (4.4) ^c				
0.1		1.3 (1.7)	1.15 (1.24)		
0.15	4.3 (5.7)				
0.2	5.2 6.8	1.5 (2.2)	1.23 (1.50)		
0.3		2.1 (3.0)	1.25 (1.74)		

^a Values of $10^5 k_{\psi}$, s⁻¹ at 25.0 °C. ^b Values are for reactions in the presence of NaCl. ^c Values are for reactions in the presence of NaBr. In water $10^5 k_{\psi} = 1.5$, 1.1, 0.8 s⁻¹ for substrates **1a**-c, respectively.

TABLE II: Reactions of Substituted Alkyl Benzenesulfonate with 0.02 M NaCl in $(CTA)_2SO_4^a$

10 ³ [(CTA) ₂ SO ₂].	substrate					
M	1a	1b	1c			
2	10 (10.5) ^b	3.8 (4.0)	3.3			
4	14 (14.5)	4.1 (4.5)	4.0			
7	14.5 (15.5)	5.2 (6.0)	4.6			
10	13 (15)	6.5 (7.5)	3.8			
30	12.2 (13)	6.8 (7.5)	3.6			
60	10.7 (10.9)	6.2 (6.4)	3.3			
100	10.2 (9.5)	5.5 (5.2)	3.2			
150	9.4 (8.5)	5.1 (4.2)	3.1			
180	8.6 (8)	4.6 (3.8)	2.9			

^a Values of $10^5 k_{\psi}$, s⁻¹ at 25.0 °C with 5 × 10⁻⁵ M substrate. ^b Values in parentheses are calculated by using the parameters in Table VI.

TABLE III: Reactions of Substituted Alkyl Benzenesulfonate with 0.02 M NaBr in (CTA)₂SO₄^a

$10^{3}[(CTA)_{3}SO_{4}]$		substrate					
	M	1a	1b	1c			
	2	43 (42.9) ^b	11 (11)	10			
	4	49 (50)	15 (16)	13			
	7	52 (54)	23 (23)	14.5			
	10	45 (48)	24 (27)	13.1			
	30	32 (38)	25 (23)	10			
	60	21 (26)	22 (19)	8			
	100	17 (22)	20 (17)	6			
	150	16 (20)	18 (15)	5			
	180	15 (17)	16 (13)	4			

^a Values of $10^5 k_{\psi}$, s⁻¹ at 25.0 °C with 5 × 10⁻⁵ M substrate. ^b Values in parentheses are calculated by using the parameters in Table VI.

The aim of the present work is to examine micellar effects upon nucleophilic substitution by Br^- or Cl^- upon substituted alkyl benzenesulfonate (1a-c) in solutions of cetyltrimethylammonium surfactant (CTAX, X = Cl, Br, OMes, 0.5SO₄) and this reaction was chosen because it is mechanistically simple, and the substrates react readily with halide ions^{10,35} (Scheme I). There is also a reaction of alkyl benzenesulfonate with water, but it is inhibited by cationic micelles such as cetyltrimethylammonium mesylate or sulfate and should make only a minor contribution under our reaction conditions.^{3,19,20}

Experimental Section

Materials. The preparation or purification of reagents and surfactants followed standard methods.^{3,19,32}

Kinetics. Reactions were followed spectrophotometrically at 25.0 °C by the decrease of absorbance at 252 nm for 1a, 262 nm for 1b, and 247 nm for 1c. The solvent was redistilled, deionized

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Figure 1. Reactions of substituted alkyl benzenesulfonate (1a-c) with Cl⁻ in CTAOMes: (0) 0.02 M NaCl with 1a, (Δ) 0.02 M NaCl with 1b, and (\odot) 0.02 NaCl with 1c.



Figure 2. Reactions of substituted alkyl benzenesulfonate (1a-c) with Br^- in CTAOMes: (0) 0.02 M NaBr with 1a, (Δ) 0.02 M NaBr with 1b, (\odot) 0.02 M NaBr with 1c.

water. Addition of 10^{-3} M HCl or HBr to the more concentrated surfactant solution did not change the rate constants, so that there was no contribution from reaction with OH⁻. The first-order rate constants, k_{ψ} , are in reciprocal seconds.

Results

Reactions in Aqueous Salts. In hydroxylic solvents Br^- is a better nucleophile than Cl^- , because hydrogen bonding reduces nucleophilicity of anions and the effect is greatest with small hydrophilic anions of high charge density.^{21,22} We see this be-

havior in our reactions (Table I). The second-order rate constants for the reactions of Cl⁻ and Br⁻ with substrate (1a-c) are 1.26 $\times 10^{-4}$ and 3.0×10^{-4} M⁻¹ s⁻¹ for substrate 1a, 2.7×10^{-5} and 6×10^{-5} M⁻¹ s⁻¹ for substrate 1b, and 2.3×10^{-5} and 3.7×10^{-5} M⁻¹ s⁻¹ for substrate 1c, respectively (no correction was made for salt effects upon these reactions).

The reactions of alkyl benzenesulfonates with halide ions were carried out in the presence of reactive and nonreactive counterion surfactants and these reactions are speeded by both surfactants.

Reactions in Nonreactive Ionic Micelles. Micellized CTAOMes or $(CTA)_2SO_4$ speeds reactions of Cl⁻ or Br⁻ with substrate (**1a-c**) (Figures 1 and 2 and Tables II and III). As is generally found, k_{ψ} goes through maxima with increasing [CTAOMes] or [(CTA)_2SO_4] and constant [anion].

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Figure 3. Reactions of substrates 1a-c in CTABr, \blacksquare , \blacktriangle , \blacklozenge , respectively. The solid lines are predicted by both model i and model ii. The open points, \square , \triangle , \bigcirc , are for the effect of CTABr + 0.1 M NaBr on the reactions of substrates 1a-c, respectively. The broken lines are calculated for model i by assuming salt effects on K_s and the solid lines are for model ii.



Figure 4. Reactions of substrates 1a-c in CTAC1. The broken lines are calculated for model i and the solid lines for model ii. Solid points, \square , \triangle , \triangle , are for reactions of 1a-c in CTAC1. Open points, \square , \triangle , \bigcirc , are for reactions of 1a-c in CTAC1. Open points, \square , \triangle , \bigcirc , are for reactions of 1a-c in CTAC1 in the presence of 0.1, 0.12, 0.08 M NaC1, respectively, and the solid lines are calculated for model ii.

Reactions in Reactive Ionic Micelles. First-order rate constants of reaction with halide ion, k_{ψ} , with respect to substrates (1a-c), increase with increasing surfactant concentration and tend to reach limiting values (Figures 3 and 4). Under some conditions, additions of the common halide ion to the surfactant solution increases k_{ψ} (Figures 3 and 4). Substrates 1a and 1c are more hydrophobic than 1b and should be more micellar bound.

Although halide ions are relatively weak nucleophiles in the absence of surfactant,^{10,18,19} we observed rate enhancements in micelles because the concentration of halide ion at the micellar

surface is greater than in the aqueous pseudophase.^{3,7}

Discussion

Reactive Counterion Surfactants. The micellar rate enhancements of reactions of substituted alkyl benzenesulfonate (1a-c) can be treated quantitatively by considering the distribution of both reactants between aqueous and micellar pseudophases and the rate constants in each pseudophase²³ (Scheme II). There is

SCHEME II



also a reaction with water which make a (minor) contribution, $k_{\rm H_2O}$, to the observed rate constant^{19,20} and we did not correct for it.

Based on Scheme II, the overall rate constant is given by eq 3^{23} where K_s is the binding constant of substrate to micelles written

$$k_{\psi} = \frac{k'_{W} + k'_{M}K_{s}[D_{n}]}{1 + K_{s}[D_{n}]}$$
(3)

in terms of the concentration of micellized surfactant and k'_{W} and $k'_{\rm M}$ are respectively the first-order rate constants in the aqueous and micellar pseudophases. The first-order rate constants can be written in terms of the second-order rate constants, $k_{\rm W}$ and $k_{\rm M}$, with the appropriate units of concentration, and for $k_{\rm M}$ we define the concentration of halide ion, X⁻, in the micelle as a mole ratio10,13,18

$$k'_{\mathbf{W}} = k_{\mathbf{W}}[\mathbf{X}_{\mathbf{W}}] \tag{4}$$

$$k'_{\rm M} = k_{\rm M} m_{\rm X}^{\rm s} = k_{\rm M} [{\rm X}_{\rm M}] / [{\rm D}_{\rm n}] = k_{\rm M} \beta$$
 (5)

where m_X^s is the mole ratio which equals β for a reactive ion surfactant.¹³⁻¹⁸ Equations 3-5 gives eqs 6, 7, 8, where subscript

$$k_{\psi} = \frac{k_{\rm W}[{\rm X}_{\rm W}^{-}] + k_{\rm M}K_{\rm s}\beta[{\rm D}_{\rm n}]}{1 + K_{\rm s}[{\rm D}_{\rm n}]}$$
(6)

$$=\frac{k_{\rm W}([{\rm X}_{\rm T}^{-}] - \beta[{\rm D}_{\rm n}]) + k_{\rm M}K_{\rm s}\beta[{\rm D}_{\rm n}]}{1 + K_{\rm s}[{\rm D}_{\rm n}]}$$
(7)

$$=\frac{k_{\rm W}([{\rm X}_{\rm T}^{-}] - [{\rm X}_{\rm M}^{-}]) + k_{\rm M}K_{\rm s}[{\rm X}_{\rm M}^{-}]}{1 + K_{\rm s}[{\rm D}_{\rm n}]}$$
(8)

T denotes the total concentration of X⁻. If β is independent of the concentration of surfactant or added reactive ion $X^{-,7,24}$ then eq 8 reduces to eq 9

$$k_{\psi} = k_{\rm M}\beta \tag{9}$$

This behavior is found for some reactions in reactive ion surfactants, e.g., in CTACN¹⁴ and CTABr^{10,18} and in some sulfonic acids.13 The rate-surfactant profiles for these reactions can be analyzed on the assumption that β is constant.^{10,13,14,19} However, this assumption fails when the counterion is small and of high charge density, e.g., OH^- , F^- , or HCO_2^- . Counterion (X⁻) distribution between aqueous and micellar pseudophases can be fitted to eq 10, i.e., to a mass-action model.¹⁵⁻¹⁷

$$K'_{X} = [X_{M}^{-}] / [X_{W}^{-}] ([D_{n}] - [X_{M}^{-}])$$
(10)

Equation 10 predicts that the fraction β of micellar head groups neutralized by counterions will increase with increasing [surfactant], although β will not vary much with [surfactant] if K'_X is large, e.g., $\geq 10^3$ M⁻¹. Thus the approximation of a constant β is probably satisfactory for an ion such as Br⁻, which binds strongly to cationic micelles, but it may fail for Cl^- , which binds less strongly than Br^- to micelles.^{6,10,25} Therefore, in treating our data

TABLE IV: Rate and Equilibrium Constants for Reactions in CTACl^a

medium	sub- strate	model ^b	<i>K′</i> _x , Μ ⁻¹	K _s , M⁻	10 ⁴ k _M , s ⁻¹	${k_2^m}/{k_w}$
CTACI	1a	i		120	2.8	0.30
CTACI	la	ii	230	120	2.9	0.32
CTACI + 0.08 M NaCl	1a	ii	230	130	2.75	0.30
CTACI	1b	i		50	1.6	0.8
CTACI	1b	ii	220	70	1.5	0.8
CTACI + 0.12 M NaCl	1b	ii	220	70	1.8	0.9
CTACI	lc	i		120	1	0.6
CTACI	1c	ii	220	120	1.1	0.66
CTACI + 0.1 M NaCl	1c	ii	220	130	1.1	0.66

^aCalculated with cmc of 1.3×10^{-3} . ^bModel i assumes a constant β of 0.8, and model ii is a mass-action treatment with variable β .

TABLE V: Rate and Equilibrium Constants for Reactions in CTABr^a

medium	sub- strate	model ^b	<i>Κ'</i> _x , M ⁻¹	<i>K</i> _s , M ⁻¹	10 ⁴ k _M , s ⁻¹	k2 ^m / k _w
CTABr	1a	i		120	8	0.37
CTABr	la	ii	2000	120	8	0.37
CTABr + 0.1 M NaBr	1a	i		120	9.4	0.43
CTABr + 0.1 M NaBr	1a	ii	2200	120	9.2	0.42
CTABr	1b	i		65°	7.3	1.7
СТАВг	1b	ii	2200	65	6.1	1.4
CTABr + 0.1 M NaBr	1b	i		65	6.2	1.5
CTABr + 0.1 M NaBr	16	ii	2300	65	6.1	1.4
CTABr	1c	i		120	3.5	1.6
CTABr	1c	ii	2200	120	3.4	1.6
CTABr + 0.1 M NaBr	1c	i		120	3.5	1.6
CTABr + 0.1 M NaBr	le	ii	2300	120	3.4	1.6

^aCalculated with cmc of 8×10^{-4} M for CTABr. ^bModel i assumes a constant β of 0.8, and model ii is a mass-action treatment with variable β . ^c The fit assumes a salt effect on substrate binding; see text.

we use two models: (i) ion-exchange mod l, where β is constant over a wide range of surfactant or halide ion concentration, as is often assumed;⁷ (ii) mass-action model, where β increases with increasing halide ion concentration, i.e., similar to micellar binding or relatively hydrophilic anion.^{10,15-17,30}

Equation 7 (model i) with constant β fits the variation of k_{μ} with [CTABr] or [CTACl] (Figures 3 and 4), using the parameters in Tables IV and V. A fundamental problem in this fitting procedure is that the rate of data can be fitted to other combinations of these parameters provided that the variations are small.9 However, in some cases k_{ψ} increases with added NaBr^{10,19} contrary to the assumption of constant β .

This discrepancy has been attributed in some cases to an increase in K_s by "salting out" of the substrate from the aqueous pseudophase. There is precedence for such an effect,⁸⁻¹⁰ but it is too small to explain all our salt effects. Therefore, at least for reaction of Cl⁻, we cannot accommodate all our data in terms of a constant β .

The alternative explanation is that β increases with increasing halide ion eq 10 (model ii). Equation 10 places formal limits of 0 and 1 on β , although the lower limit cannot be reached because there are always counterions present in the aqueous pseudophase, and the upper limit of 1 is reached only at [counterion] beyond any reasonable limit.^{15,16,19,30} In practice β varies little with [X⁻] if $K'_X \ge 10^3 \text{ M}^{-1.16}$

Equations 3 and 10 were combined by a single computer program which allowed us to simulate the variation of k_{ψ} with [CTABr] or [CTACl], and we were able to fit all the rate data for reactions in the reactive ion surfactant, and with added salt (Figures 3 and 4), using the parameters given in Table IV and v based on model ii.

For reaction in CTABr with added NaBr, the rate constants could be fitted to model i (Figure 3) assuming that NaBr salts

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TABLE VI: Rate and Equilibrium Constants for Reactions in CTAOMes and $(CTA)_2SO_4{}^{\sigma}$

medium	sub- strate	K _y ^x	<i>К</i> _s , М ⁻¹	10 ⁴ k _M , s ⁻¹	$\frac{k_2^m}{k_w}$
CTAOMes + 0.02 M NaBr	la 1b	2.5 2.5	120 65	15 2.5	0.23 0.23
CTAOMes + 0.02 M NaCi	lc la	2.5 2	120 115	1.75 1.6	0.66
$0.5(CTA)$ SO ± 0.02 M NaBr	ID 1c	2	65 120	0.8 0.6	0.41
$0.5(CTA)_2SO_4 + 0.02$ M NaBl	1b 19	90 90 65	80 150	2.75	0.28
0.5(C177)2004 1 0.02 M Nucl	1b	65	80	0.8	0.41

out the substrate from the aqueous pseudophase,^{8,9} i.e., increasing K_s following eq 11, with $b = 12 \text{ M}^{-1}$ for substrates **1a** and **1c** and **b** = 8 M⁻¹ for substrate **1b**.

$$K_{\rm s} = Z(1 + b[{\rm NaBr}]) \tag{11}$$

where Z is a constant that equals 100 for substrate 1a and 1c and 65 for substrate 1b. However, the data could be fitted reasonably well to the mass-action model ii, without making this assumption (Figure 3).

Although assumption of constant β (model i) is satisfactory for reactions in CTACl, CTABr, and CTABr + NaBr, we could not fit the rate data for reaction in CTACl + NaCl in terms of this model without taking unreasonable high values of b, eq 11, of greater than 35 M⁻¹.

We therefore conclude that β for CTACl increases with increasing [Cl⁻], although the effect is much smaller than that usually observed with CTAOH and CTAF.^{13,15–17}

Unreactive Counterion Surfactants. The maxima in k_{ψ} with increasing [CTAOMes] or [(CTA)₂SO₄] and constant [Cl⁻] or [Br⁻] (Figures 1 and 2, Tables II and III) are typical of micellar rate enhancements with varying concentrations of inert surfactant and a constant [nucleophile].¹⁻⁷ The rate-surfactant profile for reactions in CTAOMes can be treated quantitatively by using the pseudophase ion-exchange model based on eq 2, with the concentration of micellar-bound nucleophilic anion calculated by using the ion-exchange equilibrium, eq 2.³⁻⁷

The general approach in fitting the variation of k_{ψ} with [surfactant] or salt is to use eq 2 and the mass balance relation, with assumed values of $K_{\text{Mes}}^{\text{O}}$ to calculate $[X_{\text{M}}^{-}]$ and $[X_{\text{W}}^{-}]$ and to insert these values into the rate equation by using assumed values of k_{M} and K_{s} and the measured k_{W} and to simulate the variation of k_{ψ} with [CTAOMes] for example.

Our data in CTAOMes could be fitted by taking K_{OMes}^{Br} and $K_{OMes}^{Cl} = 2.5$ and 2 M⁻¹, respectively, for all the added anions and we took $\beta = 0.7-0.8^{.3.4,10,27}$ 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., 120 for substrates **1a** and **1c** and 65 for substrate **1b** respectively (Figures 1 and 2). Variations of cmc or K_s had no effect on the predicted rate surfactant profiles except in very dilute surfactant. The values of the parameters used to fit our data in CTAOMes are given in Table VI.

We attempted to calculate the variation of k_{ψ} with the [CTA⁺] which is equal to 0.5 [(CTA)₂SO₄] using the ion-exchange model i. In our calculation we took $K_{SO_4}^{Br}$ and $K_{SO_4}^{CI} = 90$ and 65 M⁻¹, respectively; these values are very close to those in the literature,^{33,34} and we took $\beta = 0.9$ and $K_s = 150$ M⁻¹ for substrate **1a** and 80

 M^{-1} for substrate 1b. Tables II and III show the experimental and calculated values for substrates (1a-c). These calculations were done using the parameters in Table VI.

Rate Constants in the Micelle. The pseudophase description of micellar rate effects involves the implicit assumption that micelles provide a discrete reaction environment, and on this basis we attempt to compare rate constants in this environment with those in water. This comparison will be misleading for multistep reactions if micelles change the rate-limiting step or a preequilibrium,^{35,36} but this should not be a problem for S_N2 reactions.

The second-order rate constants in a homogeneous solvent are typically expressed as $M^{-1} s^{-1}$ and cannot be compared directly with k_M , where concentration is written as a mole ratio. Second-order rate constants in micellar phase with same dimensions k_2^m , $M^{-1} s^{-1}$, are given by

$$k_2^{\rm m} = k_{\rm M} V_{\rm M} \tag{12}$$

where $V_{\rm M}$ is the molar value of the reactive region at the micellar surface, and we take $V_{\rm M} = 0.14$ L mol⁻¹ on the basis of earlier estimates.^{3,7,13-17}

The values of k_2^m for reactions in the micellar stern layer are almost identical with those of k_w in water (Tables IV, V, and VI). The close similarity is probably coincidental, because it depends upon our estimated molar volume of the Stern layer. However, the overall volume of the micelle is probably approximately twice that of the Stern layer,^{3,7} so our overall conclusion would be little affected by the choice of a different volume elements of reaction.

The similarity of k_2^m and k_w is understandable, because all substrates and halide ions should be located near the water-rich micellar surface.^{3,7,29} There are many examples of reactions for which second-order rate constants in micelles are similar to those in water, and the differences in constants are probably due to the properties of the micelle as a kinetic solvent, or to a different location of the reactants in the micelle.

Comparison of the Models. The rate-surfactant profiles for reactions in CTAOMes or $(CTA)_2SO_4$ can be fitted to model i (Figures 1 and 2 and Tables II, III, and VI). The rate-surfactant profiles for reactions in CTABr or CTACl can be fitted to either model i or ii (Figures 3 and 4) (Tables IV and V). The variations of k_{ψ} with [CTABr] + 0.1 M NaBr can be fitted to mass-action model, eq 10, by taking $K'_{Br} = 2200 \text{ M}^{-1}$ (Table V). The values of K'_X for Cl⁻ (Table IV) are reasonable, in comparison with K'_{OH} = 55 M⁻¹ and $K'_{For} = 80 \text{ M}^{-1}$ formate and acetate ions,¹³⁻¹⁷ because less hydrophilic ions such as Cl⁻ or Br⁻ should have larger binding constants. The values of K_s and k_M are similar for both models. These comparisons suggest that estimation of K_M is relatively straightforward and insensitive to the model chosen for treatment of the data.

However, the competition between SO_4^{2-} and Br^- or Cl^- provides evidence for a more complex behavior.³³ On the other hand, it has been determined that the selectivity coefficients for monovalent/divalent counterion exchange indicate that the relative binding affinities for counterions are similar to those observed when these ions participate in competitive divalent/divalent or monovalent/monovalent exchange.^{25,33} However, studies on $SO_4^{2^-}/Br^$ suggest that this is not general to all divalent/monovalent counterion exchanges.³³

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