Hammett Equation and Micellar Effects upon Deacylation

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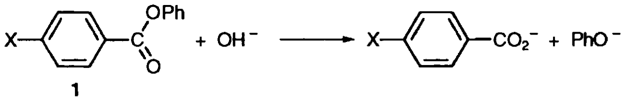
Substituent effects upon second order rate constants of reaction of OH^- with phenyl *p*-substituted benzoates at surfaces of micelles of cetyltrialkylammonium bromide (alkyl = Me, Et, Pr and Bu) and tetradecylquinuclidinium bromide fit the Hammett equation. Values of ρ increase with increasing bulk of the surfactant head group and are considerably larger than in water, corresponding to decreases in micellar surface polarity. The effects of substitution of the propyl group into the phenyl and benzoyl groups show that substrate orientation at micellar surfaces plays no significant kinetic role.

Aqueous micelles and similar association colloids can increase rates of bimolecular reactions by concentrating both reactants at the surfaces of the colloids.[1] Reactant concentrations at these surfaces can be determined experimentally,[2] or estimated,[1,3] and second order rate constants can then be calculated. Most work has involved micelles, which are treated as a reaction medium, distinct from bulk solvent. For many reactions of nucleophilic anions second order rate constants at surfaces of cationic micelles are similar to, and often slightly lower than, second order rate constants in water.[1] However, differences in these rate constants seem to be related to differences in reaction mechanism and reactant structure, for example, second order rate constants of reactions of OH^- with aryl benzoates are considerably lower at micellar surfaces than in water.[1,4,5] Early results, based on overall rate constants of reactions of OH^- with carboxylic esters, showed that electron withdrawing groups increase rate constants in micellar solutions relative to those in water.[1,6] This conclusion seems to apply to a variety of reactions of nucleophilic anions and Correia *et al.* used a pseudophase ion exchange (PIE) model to estimate second order rate constants of reactions of OH^- with substituted phenyl benzoates at the surface of micelles of cetyltrimethylammonium bromide.[4] Second order rate constants in water and at the micellar surface fitted the Hammett equation, based on σ_p parameters and for substituents in the benzoyl residue $\rho = 1.86$ and 2.65 in the aqueous and micellar pseudophases respectively. Application of the Hammett equation to acid hydrolysis in anionic micelles is given in ref. 6, with other examples of the application of the Hammett equation given in ref. 4, although some are based on rate constants for overall reaction, so ρ values depend upon transfer equilibria as well as rate constants.

We initially examined substituent effects in the benzoyl group for reactions mediated by micelles of cationic surfactants (Scheme 1).



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a X = H
b X = OMe
c X = Me
d X = Cl
e X = CN

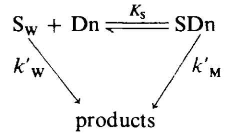
Scheme 1

We did not examine nitro derivatives because they are too reactive for their reactions to be followed conveniently in solutions of OH^-, and we chose to avoid buffers. The surfactants were cetyltrialkylammonium bromide, $C_{16}H_{33}NR_3Br$ (R = Me, CTABr; R = Et, CTEABr; R = Pr, CTPABr; R = Bu, CTBABr), and tetradecylquinuclidinium bromide, $C_{14}H_{29}NC_7H_{13}Br$, TDQBr. Reactions of most of the esters were followed in 0.1 mol dm^{-3} OH^-, although that of cyano derivative (**1e**) was followed in 0.01 mol dm^{-3} OH^- and for the chloro derivative (**1d**) we used both 0.01 and 0.1 mol dm^{-3} OH^-. Data for reaction of phenyl benzoate are given in ref. 5.

There has been discussion of possible rate effects due to substrate orientation at a micelle–water interface,[7] and although it could have complicated analysis of substituent effects, substrate orientation did not affect results with aryl benzoates[4a] and with (arylsulfonyl)alkyl arenesulfonates.[4b] We examined the rate effects of substitution of a propyl group at the *para* position of the benzoyl group and at the *ortho* and *para* positions of the phenoxy group in phenyl benzoate. The propyl and methyl groups should have very similar electronic effects, but the propyl group should increase substrate hydrophobicity and might influence substrate orientation at the micellar surface.

A major problem in analysing medium effects upon bimolecular, non-solvolytic reactions is that second order rate constants have the dimensions of reciprocal concentration, reciprocal time. Concentrations in solution are often written as molarities, *i.e.*, mol dm^{-3}, and second order rate constants of solution reactions are then expressed with units of s^{-1} mol^{-1} dm^3. This choice of concentration units conditions our interpretation of medium effects upon rates of second and higher order reactions.

Reaction rates in micelles, and in similar colloidal assemblies, can be analysed quantitatively in terms of the pseudophase model (Scheme 2),[1] where substrate S_W, in water, complexes with micellised surfactant (detergent), Dn, forming SDn with an association constant, K_S.



Scheme 2

Reaction occurs in the aqueous or micellar pseudophases, with first order constants, k'_W and k'_M respectively. The first order rate constant for overall reaction, k_{obs}, is given by eqn. (1).[1]

$$k_{obs} = \frac{k'_W + k'_M K_S[\mathrm{Dn}]}{1 + K_S[\mathrm{Dn}]} \tag{1}$$

Micellar rate effects upon spontaneous water-catalysed reactions can be treated unambiguously in terms of eqn. (1), because first order rate constants are independent of concentration, so fitting of rate data requires only estimation of K_S for transfer of S between water and micelles. The problem is more difficult when a second reagent is involved, as in reactions of OH^-, because k'_W and k'_M depend on concentrations of OH^- in both water and micelles. Therefore we have to consider the transfer equilibrium of OH^- and the appropriate units of concentration in each pseudophase. The concentration of OH^- at a micellar surface can be written as a mole ratio of bound OH^- to micellar head groups, but then second order rate constants in aqueous and micellar pseudophases cannot be compared directly, because of differences in concentration units. Alternatively we can write concentration in the micellar pseudophase as a local molarity, in which case two questions arise: (i) is molarity the appropriate measure of concentration in a micelle, and (ii) how should we estimate the volume of the reaction region in the micelle? The answer to the first question is as obscure for micelles as it is for solutions, and the volume of the micellar reaction region can be identified with that of the whole micelle, or with an interfacial region at the surface.[1]

These problems are less serious if we consider only rate effects of a given surfactant, *e.g.*, one with a trimethylammonium head group, for reactions of OH^-, although even here the volume of the reaction region may depend upon the nature of the reactants. The problem is more difficult if we vary the head group. We are interested in the extent to which changes in head group size affect micellar surfaces.[5,8] A size increase from trimethyl- to tributyl-ammonium, for example, increases fractional micellar ionisation, α,[2d,9] and the decreased ionic concentration at the surface should decrease overall rates of bimolecular ionic reactions. This inhibition may be offset by changes in the properties of the surface as a submicroscopic reaction region. For example, bulky alkyl groups may exclude water from the interfacial reaction region and increase rates by decreasing polarity or ionic hydration.[5,8,9] However, analyses of these effects of head group size depend upon the transfer equilibrium of the ionic reagent and estimation of ionic concentration at the micellar surface.[1]

We had examined the reaction of phenyl benzoate with OH^- in solutions of micellised surfactants with different sized cationic head groups. Based on analysis of rate-surfactant profiles we concluded that second-order rate constants at micellar surfaces were considerably lower than in water, in agreement with other results,[4] but these rate constants decreased only slightly with increasing head group bulk.[5]

For reactions of OH^- eqn. (1) can be written as eqn. (2) where

$$k_{obs} = \frac{k_W[OH_W^-] + k_M K_S[OH_M^-]}{1 + K_S[Dn]} \qquad (2)$$

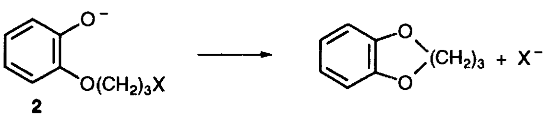
$[OH_W^-]$ and $[OH_M^-]$ are molarities in the aqueous and micellar pseudophases, respectively, written in terms of the total solution volume, k_W ($dm^3\ mol^{-1}\ s^{-1}$) is the second order rate constant in water and k_M (s^{-1}) is that in the micellar pseudophase with concentration written as the mole ratio, $[OH_M^-]/[Dn]$. Alternatively eqn. (2) can be written in terms of the local molarity of OH^- at the micellar surface, OH_M^-, which is related to $[OH_M^-]$ by eqn. (3)[1] which leads to eqn. (4) and $k_2^m = k_M V_M$ where V_M ($mol^{-1}\ dm^3$) is the partial molar volume of the interfacial reaction region in the micellar pseudophase. The attractive feature of eqn. (4) is that k_W and k_2^m are written in the same units of concentration and can therefore be compared numerically. But the numerical value of OH_M^-, and k_2^m depend linearly on V_M, whose value can only be inferred.

$$OH_M^- = [OH_M^-]/([Dn]V_M) \qquad (3)$$

$$k_{obs} = \frac{k_W[OH_W^-] + k_2^m K_S[Dn]OH_M^-}{1 + K_S[Dn]} \qquad (4)$$

The value of V_M is sometimes taken to be that of the micelle, which is unrealistic because ionic reagents should not penetrate the micellar core. An alternative assumption is that the reaction region is the micellar Stern layer, and its molar volume may depend upon the size of the surfactant head groups, and perhaps the nature of the reaction.[1]

As a result of this uncertainty in V_M it is reasonable to base conclusions regarding head group size and reactivity on values of k_M, *i.e.*, with concentration written as a mole ratio. As noted earlier, for reaction of OH^- with phenyl benzoate k_M decreases slightly with increasing head group size,[5] which has essentially no effect upon rate constants of the S_N2 reaction of OH^- with methylnaphthalene-2-sulfonate.[10] However, for reactions of OH^- with 1-chloro-2,4-dinitronaphthalene and of halide ions with methylnaphthalene-2-sulfonate, k_M increases with increasing head group size.[9b,11] The spontaneous cyclisation of **2** (Scheme 3) involves an S_N2-like transition state, and micellar effects upon reaction rate can be defined unambiguously without consideration of the distribution of a second reagent [eqn. (1)].[8a]



2

X = Br, I

Scheme 3

First order rate constants, k'_M, of this cyclisation increase by factors of *ca.* 4 (X = Br) and *ca.* 8 (X = I) with a change from the trimethyl- to the tributyl-ammonium head group.

Analyses of rate data as applied to effects of head group size depend upon various assumptions and we sought a less ambiguous way of monitoring the properties of surfaces of cationic micelles. Electronic substituent effects often depend upon solvent.[12] For example, Hammett ρ values generally become more positive as the polarity and water content of solvents are decreased. Micellar effects upon ρ values of reactions of anionic nucleophiles are consistent with polarities of micellar surfaces being lower than that of water,[1,4] in agreement with evidence based on spectral probes.[13]

If an increase in the size of cationic micellar head groups decreases polarity and the availability of water in the interfacial region, ρ should be more positive for micellar than for water reactions. The advantage of this approach over others is that values of ρ depend upon relative free energies of activation and differences in reactivities are unaffected by assumptions regarding V_M or other fitting parameters which impair comparisons of k_M, or k_2^m [eqns. (2)–(4)].

Results and Discussion

Reactions of OH^- with substituted phenyl benzoates in solutions of CTABr had been followed in solutions of OH^- for the less reactive substrates and in various buffers, at lower pH, for the more reactive substrates.[4] Second order rate constants at the micellar surface were calculated in terms of the PIE model which allows for competition between OH^- and inert anions for the micelle and assumes that its fractional ionisation, α, is constant, *i.e.*, that ions exchange at the micellar surface on a one for one basis.[1,3a,b] Thus calculated rate constants depend upon values of α and the ion-exchange constants. We avoided use of buffers by following all reactions in solutions of OH^-.

Table 1 Second order rate constants in water and micelles[a]

Compound	Substituent	H_2O	CTABr	CTEABr	CTPABr	CTBABr	TDQBr
1a	H[b]	39.0	8.5	6.5	5.0	6.0	7.5
1b	MeO	11.0 (0.28)	1.4 (0.16)	0.9 (0.14)	0.6 (0.12)	0.5 (0.095)	1.1 (0.15)
1c	Me	20.0 (0.51)	3.0 (0.35)	2.2 (0.34)	1.7 (0.34)	1.8 (0.30)	2.7 (0.36)
1d	Cl	96.0 (2.5)	39.0 (4.6)	28.0 (4.3)	25.0 (5.0)	33.0 (5.5)	30.0 (5.1)
1e	CN	637 (14)	550 (65)	470 (72)	550 (110)	720 (120)	

[a] At 25.0 °C. Second order rate constants in water are $k_W/10^{-2}$ s^{-1} mol^{-1} dm^3, those in the micellar pseudophase are $k_M/10^{-2}$ s^{-1}. Values in parentheses are relative to rate constants for phenyl benzoate (**1a**). [b] Ref. 5.

Table 2 Effect of the propyl group on second order rate constants[a]

Substituent	H_2O	CTABr	CTEABr	CTBABr	TDQBr
H	39.0	8.50	6.50	6.00	7.50
p-Me	20.0 (0.51)	3.00 (0.35)	2.20 (0.34)	1.80 (0.30)	2.70 (0.36)
p-Pr	16.0[b] (0.40)	3.00 (0.35)	2.20 (0.34)	1.80 (0.30)	2.21 (0.29)
p-Pr′	20.7[c] (0.53)	4.93 (0.58)	3.57 (0.55)	2.57 (0.43)	3.57 (0.48)
o-Pr′	14.5[c] (0.37)	4.07 (0.48)	3.21 (0.49)	2.07 (0.35)	3.21 (0.43)

[a] At 25.0 °C and 0.1 mol dm^{-3} OH^- unless specified (Experimental). Second order rate constants in water are $k_W/10^{-2}$ s^{-1} mol^{-1} dm^3 and in micelles are $k_M/10^{-2}$ s^{-1}. The prime indicates substitution in the phenoxy group. Values in parentheses are relative to reaction of phenyl benzoate. [b] Approximate value by comparison of rate constants in a mixed solvent. [c] By extrapolation from higher temperatures.

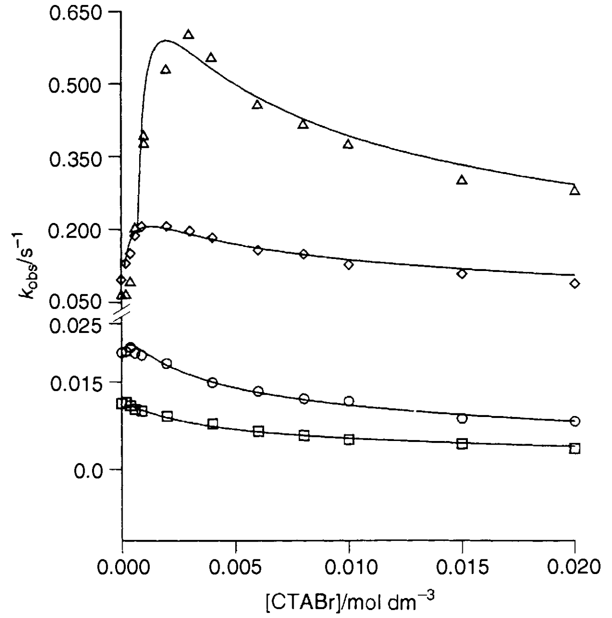


Fig. 1 Reactions in CTABr and 0.1 mol dm^{-3} OH^- except for reaction of the *p*-cyano derivative (**1e**) with 0.01 mol dm^{-3} OH^-. *p*-Substituents: (□) OMe; (○) Me; (◇) Cl; (△) CN.

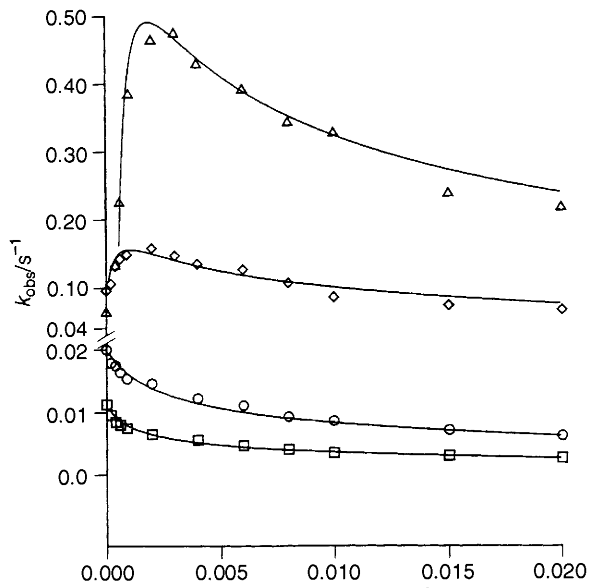


Fig. 2 Reactions in CTEABr. Symbols as in Fig. 1.

Rate data for reaction of OH^- with phenyl benzoate in solutions of various cationic surfactants had been fitted in terms of a pseudophase model [eqns. (2)–(4)],[5] in which the distribution of OH^- between the aqueous and micellar pseudophases is written in terms of the mass-action-like eqns. (5) and (6).[1c,3cd,14]

$$K'_{OH} = [OH^-_M]/[OH^-_W]([Dn] - [OH^-_M] - [Br^-_M]) \quad (5)$$

$$K'_{Br} = [Br^-_M]/[Br^-_W]([Dn] - [OH^-_M] - [Br^-_M]) \quad (6)$$

This treatment differs from the classical ion-exchange model in that it does not require constancy of α. Eqns. (2)–(6) were combined and the micellar rate effects were simulated based on the parameters in Table 1. The application of these equations and values of K'_{OH} and K'_{Br} have been discussed.[5,8b,14]

The second order rate constant, k_M, can be calculated unambiguously in terms of the pseudophase model and the parameters in eqns. (2), (5) and (6). Values of K'_{OH} and K'_{Br} (Experimental) are those used earlier for fitting data on reactions of OH^- with phenyl benzoate and other substrates.[5] Fits are sensitive to the value K'_{OH} and to a lesser extent to that of K'_{Br}, but for these hydrophobic esters fits are insensitive to values of K_S. Values of ρ from plots of log k_M against σ_p should be insensitive to values of fitting parameters such as K'_{OH}, K'_{Br} and V_M because, even if they are incorrect, errors should cancel to a first approximation, and k_M is calculated for solutions containing only OH^- and Br^- as competing anions.

Second order rate constants in aqueous and micellar pseudophases for reactions of OH^- with substituted phenyl benzoates are in Table 1 and those for reactions of the propyl derivatives are in Table 2. These rate constants are based on the rate constant-surfactant profiles (Figs. 1-5 and Supplementary Tables 1–11).*

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* Supplementary publication 56996. For details of the deposition scheme see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, issue 1, 1994.

Table 3 Values of ρ for reactions in water and aqueous surfactants[a]

Reaction medium	H_2O	CTABr	CTEABr	CTPABr	CTBABr	TDQBr
ρ	1.76	2.63	2.73	2.96	3.13	2.83
Correlation coefficient	0.9993	0.9986	0.9988	0.9988	0.9963	0.9993

[a] Calculated by a linear least square fit from data in Table 2 and σ values in ref. 12*b*, *c*.

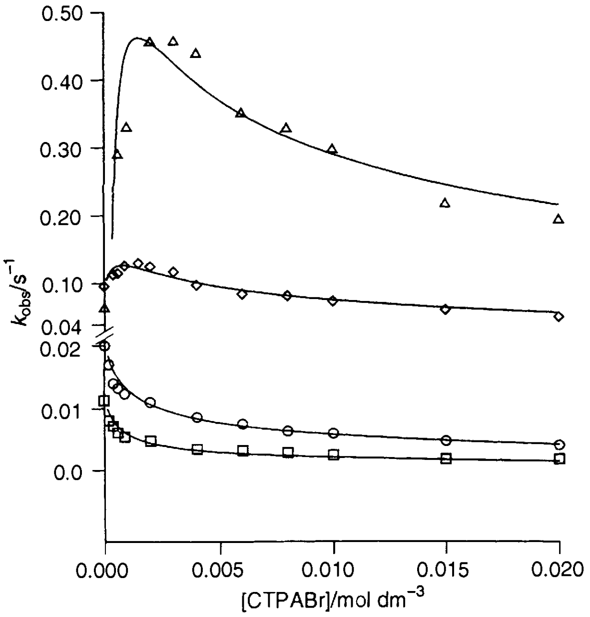

Fig. 3 Reactions in CTPABr. Symbols as in Fig. 1.

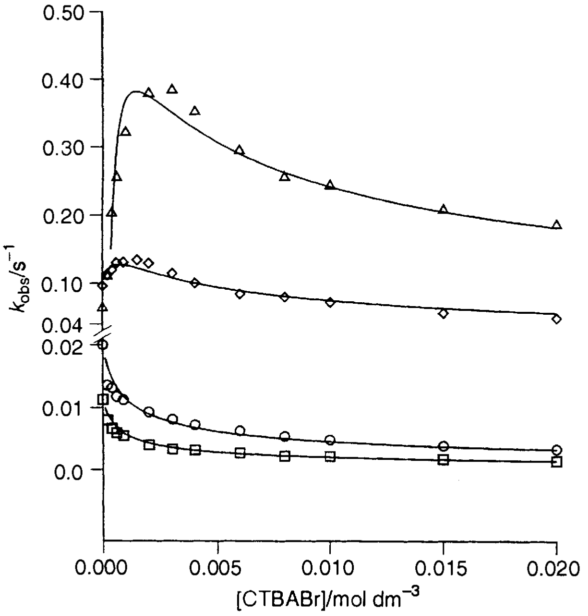

Fig. 4 Reactions in CTBABr. Symbols as in Fig. 1.

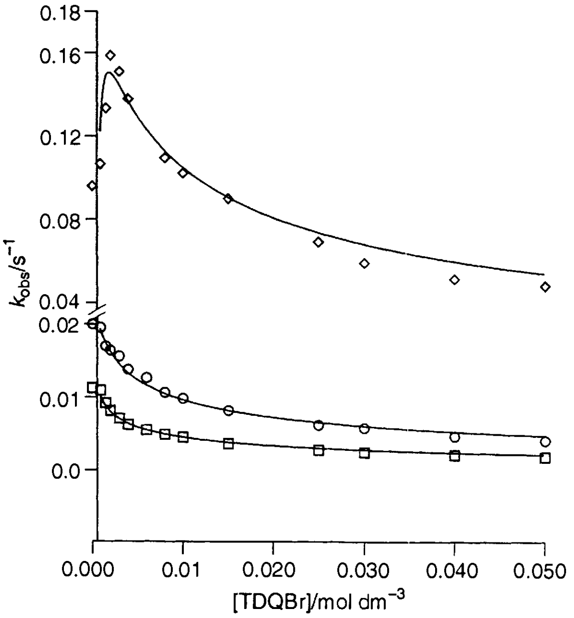

Fig. 5 Reactions in TDQBr. Symbols as in Fig. 1.

Rate constants in aqueous and micellar pseudophase fit the Hammett equation with $\sigma_p = -0.28$; -0.16; $+0.22$ and $+0.71$ for OMe, Me, Cl and CN, respectively.[12b,c] Values of ρ increase sharply with a change from water to aqueous surfactants and less sharply in the sequence CTABr, CTEABr, TDQBr, CTPABr, CTBABr (Table 3).

Electronic Effects in Aqueous and Micellar Pseudophases.— Our results agree with those of Correia *et al.*[4] in showing that electronic effects on deacylation by OH^- increase in changing the reaction medium from water to a cationic micelle. It is reasonable to relate this effect to the lower polarity of micellar surfaces, as compared to water, based on analogies with solvent effects upon values of ρ.[12] This dependence of ρ upon medium polarity is rationalised by qualitative descriptions of medium effects upon rates of organic reactions and generalisations applied to reactions in homogeneous solutions, extended to reactions in micellar pseudophases.[4,5]

The increase of ρ with increasing the bulk of the surfactant head group shows that surface polarity decreases as the size of the *N*-alkyl group is increased, as had been suggested earlier, based on kinetic and NMR data.[5,8–11] There is no evidence that orientation of the substrate at the micellar surface is kinetically significant, based on comparison of rate data for propyl and methyl derivatives (Table 2), so the fits to the Hammett equation are not an artefact of substituent effects upon substrate orientation.

Our value of ρ for deacylation in CTABr micelles at 25.0 °C is very similar to that of 2.65 for the corresponding reactions at 30 °C, although the latter value was derived from data in different buffers and in OH^-.[4]

Differences in ρ for reactions in water and at the micellar surfaces are more informative than raw rate data in analysing medium effects of micelles and similar assemblies on reactivity. We can compare k_W and k_2^m if we write concentration of OH^- as moles per unit of volume of reactive region at the micellar surface.[3] There is uncertainty in values of V_M,[1] although it is usually assumed to be in the approximate range 0.14–0.37 mol^{-1} dm^3. We have used the lower value in fitting data,[1c] although there is no assurance that it is independent of the nature of the reaction or the size of the head group.[5,16] This problem is general for second order reactions in solution, even in the

Table 4 Relative second order rate constants in water and micelles[a]

Substituent	CTABr	CTEABr	CTPABr	CTBABr	TDQBr
H[b]	0.030	0.023	0.018	0.021	0.027
MeO	0.018	0.012	0.007	0.006	0.014
Me	0.021	0.016	0.012	0.012	0.019
Cl	0.057	0.041	0.036	0.048	0.044
CN	0.12	0.10	0.12	0.16	

[a] Values of k_2^m/k_W with $V_M = 0.14$ mol^{-1} dm^3. [b] Ref. 5.

absence of colloidal assemblies, because the choice of concentration unit is arbitrary. Comparisons of k_W/k_2^m, based on $V_M = 0.14$ mol^{-1} dm^3, show that electron withdrawing groups favour reaction in micelles relative to water, especially when the surfactant has a bulky head group, *e.g.*, N^+Bu_3 (Table 4). We cannot compare trialkyl and quinuclidinium bromides with the hexadecyl residue because of solubility problems, but the bicyclic quinuclidinium group behaves very much like the N^+Me_3 and N^+Et_3 groups in its effect on reactivity.[5]

Effects of propyl groups. Methyl and propyl groups should have very similar electronic effects so comparison of the rate constants in the micellar pseudophase provides information on the effects of substrate location and orientation at the micelle–water interface.[7] For all the surfactants studied second order rate constants in the micellar pseudophase are similar for phenyl *p*-methyl- and *p*-propyl-benzoates (Table 2). Introduction of a propyl group into the phenoxy group in either the *ortho* or *para* position slows reaction in both aqueous and micellar pseudophases, as expected for an alkyl substituent, but there are no significant differences in relative rate constants in pseudophases for the four surfactants that we examined.

These results indicate that the propyl group does not control substrate orientation at the micellar surface, or that orientation has little effect upon reactivity in the micellar pseudophase. Broxton and co-workers have evidence for orientational effects in nucleophilic aromatic substitution in cationic micelles,[7a] so the behaviour may be governed by the geometry of the substrate. There are a number of examples of reactions in which micelles affect product composition.[1b,17] In some cases competing reactions have different kinetic orders, so it is then easy to understand micellar effects on products, but in others products may be controlled by substrate orientation or location in interfacial regions.[17e,f]

Medium effects on reactivity. In ester saponification the structure of the transition state should be similar to that of an anionic tetrahedral intermediate with charge on oxygens, Interaction with hydroxylic solvents, *e.g.*, water, should stabilise the transition state and this stabilisation will decrease in micelles. At the same time micelles and organic solvents lower the free energies of hydrophobic esters, which also inhibits reaction. However, in dry aprotic solvents dehydration of OH^- may compensate for these medium effects upon substrate and transition state. These medium effects are attenuated by strongly electron-withdrawing substituents that stabilise the anionic transition state. The widespread use of nitro derivatives in studies of nucleophilic displacements therefore conditions our views of solvent and micellar effects on reactivity.[1]

In aromatic nucleophilic substitution negative charge is delocalised in a π-system and as a result second order rate constants for reactions with OH^- are similar in aqueous and micellar pseudophases,[1,3c,e,8] in contrast to the situation for reactions of OH^- with carboxylic and phosphate esters where these rate constants are significantly higher in water than in cationic micelles.[1,4,5,14] As noted earlier these comparisons depend upon assumptions in treatments of the micellar data, but estimation of concentrations of OH^- by solution of the Poisson–Boltzmann equation[1c–e,3e] gives results similar to those based on eqns. (5) and (6) or the PIE.[1] It appears that the simple physical-organic concepts that fit solvent effects in solution[18] also apply to micellar rate effects.[19]

Experimental

Materials.—Esters were prepared from the appropriate phenols and acid chlorides in pyridine[20] and solids were recrystallised from MeOH. The following m.p./°C, are for phenyl derivatives: *p*-Me, 77–78 (lit.,[20b] 73); *p*-OMe, 70–71 (lit.,[20c] 75); *p*-Cl, 105–106 (lit.,[20b] 105–106); *p*-CN, 92–94. The m.p./°C of *p*-propylphenyl benzoate and phenyl *p*-propylbenzoate are 39 (lit.,[20a] 37–38) and 43–45 respectively. All the esters gave single spots in TLC and had the expected ^1H NMR spectra. *o*-Propylphenyl benzoate is a liquid and after distillation *in vacuo* it gave a single GLC peak and had the expected ^1H NMR spectrum.

Preparation and purification of the surfactants are described,[5,8] and reactions were carried out in deionised and distilled, CO_2-free water.

Reactions in Water and Surfactant.—Reactions in the absence of surfactant could be followed in water,[5] except for some propyl derivatives as discussed later.

Reactions were followed spectrophotometrically at 25.0 °C, with 8×10^{-5} mol dm^{-3} substrate added in MeCN so that the reaction solution contained 0.8% v/v MeCN. The increasing absorbance was followed at 298 nm for most of the esters and the decreasing absorbance at 254 nm for phenyl *p*-cyanobenzoate. Shimadzu or HP diode array spectrophotometers were used at 25.0 °C, except where specified, and first order rate constants with respect to ester are designated k_{obs}/s^{-1}.

Reactions were carried out in 0.1 mol dm^{-3} OH^- except for phenyl *p*-cyanobenzoate whose reaction was followed in 0.01 mol dm^{-3} OH^-. We also examined reaction of phenyl *p*-chlorobenzoate in 0.01 mol dm^{-3} OH^- where $k_M = 0.39$ and 0.33 s^{-1} in CTABr and CTBABr respectively in agreement with values in 0.1 mol dm^{-3} OH^-.

Reactions of Propyl Derivatives.—Reaction of the propyl derivatives could not be followed in water at 25.0 °C, and those of *p*-propyl- and *o*-propyl-phenyl benzoate were followed at higher temperatures in water. First order rate constants 10^3 k_{obs}/s^{-1} in 0.01 mol dm^{-3} NaOH at 45.0, 50.0, 55.0 and 60.0 °C are 6.64 (4.84), 9.25 (6.48), 12.0 (8.87) and 14.9 (10.8) respectively: values in parentheses are for the *ortho* derivative. Arrhenius parameters are: *E*, 47.0 (48.3) kJ mol^{-1}; log *A*, 5.6 (5.6) and extrapolated values of 10^3 k_{obs}/s^{-1} at 25.0 °C are 2.07 (1.45).

We could not use this method for phenyl *p*-propylbenzoate because it is too insoluble in water. In NaOH (0.1 mol dm^{-3}) and H_2O:MeCN 2:1 v/v, 10^3 $k_{obs} = 1.94$ s^{-1} at 25.0 °C and under the same conditions 10^3 $k_{obs} = 2.46$ s^{-1} for phenyl *p*-methylbenzoate. We assume that the rate constant for reaction of phenyl *p*-propylbenzoate in water will be slightly lower than that of the *p*-methyl derivative and the approximate value given in Table 2 is calculated on the assumption that relative rates are similar in water and the mixed solvent.

Data Simulation.—Values of k_M were calculated by fitting rate–surfactant profiles as described.[5,14] Values of K'_{OH} are 55, 45, 25, 12 and 50 $mol^{-1} dm^3$ for CTA, CTEA, CTPA, CTBA and TDQ respectively and corresponding values of K'_{Br} are 2000, 1500, 1100, 750 and 1700 $mol^{-1} dm^3$. As in earlier simulations we took K_S = 1500, 3000, 2000, and 2000 $mol^{-1} dm^3$ for the phenoxybenzoates with *p*-substituents MeO, Me, Cl and CN respectively and 4000 $mol^{-1} dm^3$ for the propyl derivatives, but because these esters partition strongly into micelles fits are insensitive to values of K_S. Values of the kinetic cmc are, in 0.1 mol dm^{-3} OH^-, 7×10^{-5}; 3×10^{-5}; 10^{-5}; 10^{-5} and 7×10^{-4} mol dm^{-3} for CTABr, CTEABr, CTPABr, CTBABr and TDQBr respectively and values, in 0.01 mol dm^{-3} OH^-, are 7×10^{-4}, 5×10^{-4}; 4×10^{-4} and 10^{-4} mol dm^{-3} for CTABr, CTEABr, CTPABr and CTBABr respectively.

Supplementary Material

1. Tables of variations of k_{obs} with [surfactant] corresponding to Figs. 1–5.
2. Tables of variations of k_{obs} with [CTABr] and [CTBABr] for reaction of phenyl *p*-chlorobenzoate with 0.01 mol dm^{-3} NaOH.
3. Tables of variations of k_{obs} with [surfactant] at 0.1 mol dm^{-3} NaOH for reactions of phenyl *p*-propylbenzoate, *p*-propylphenyl benzoate and *o*-propylphenyl benzoate.

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References

1 (*a*) L. S. Romsted in *Surfactants in Solution*, eds. K. L. Mittal and B. Lindman, Plenum Press, New York, 1984, vol. 2, p. 1015; (*b*) E. J. R. Sudholter, G. B. van der Langkruis and J. B. F. N. Engberts, *Recl. Trav. Chim. Pays-Bas*, 1980, **99**, 73; (*c*) C. A. Bunton and G. Savelli, *Adv. Phys. Org. Chem.*, 1986, **22**, 213; (*d*) C. A. Bunton, F. Nome, L. S. Romsted and F. H. Quina, *Acc. Chem. Res.*, 1991, **24**, 357; (*e*) C. A. Bunton in *Surfactants in Solution*, eds. K. L. Mittal and D. O. Shah, Plenum Press, New York, 1991, vol. 11, p. 17.

2 (*a*) L. Sepulveda, E. Lissi and F. H. Quina, *Adv. Colloid Interface Sci.*, 1986, **25**, 1; (*b*) C. A. Bunton, K. Ohmenzetter and L. Sepulveda, *J. Phys. Chem.*, 1977, **81**, 2000; (*c*) R. Zana, *J. Colloid Interface Sci.*, 1980, **87**, 330; (*d*) P. Lianos and R. Zana, *J. Colloid Interface Sci.*, 1982, **88**, 594.

3 (*a*) F. H. Quina and H. Chaimovich, *J. Phys. Chem.*, 1979, **83**, 1844; (*b*) L. S. Romsted, *J. Phys. Chem.*, 1985, **89**, 5107, 5113; (*c*) C. A. Bunton, L.-H. Gan, J. R. Moffatt, L. S. Romsted and G. Savelli, *J. Phys. Chem.*, 1981, **85**, 4118; (*d*) E. Rodenas and S. Vera, *J. Phys. Chem.*, 1985, **89**, 513; (*e*) C. A. Bunton and J. R. Moffatt, *J. Phys. Chem.*, 1986, **90**, 538; (*f*) E. Rodenas and F. Ortega, *J. Phys. Chem.*, 1987, **91**, 837.

4 V. R. Correia, I. M. Cuccovia and H. Chaimovich, *J. Phys. Org. Chem.*, 1991, **4**, 13.

5 R. Germani, G. Savelli, N. Spreti, G. Cerichelli, G. Mancini and C. A. Bunton, *Langmuir*, 1993, **9**, 61.

6 E. H. Cordes and C. Gitler, *Progr. Bioorg. Chem.*, 1973, **2**, 1.

7 (*a*) T. J. Broxton, J. R. Christie and R. P.-T. Chung, *J. Org. Chem.*, 1988, **53**, 3081; (*b*) G. B. van de Langkruis, J. B. F. N. Engberts, *J. Org. Chem.*, 1984, **49**, 4152; (*c*) M. Witte and J. B. F. N. Engberts, *J. Org. Chem.*, 1985, **50**, 4130.

8 (*a*) G. Cerichelli, L. Luchetti, G. Mancini, M. N. Muzzioli, R. Germani, P. P. Ponti, N. Spreti, G. Savelli and C. A. Bunton, *J. Chem. Soc., Perkin Trans. 2*, 1989, 1081; (*b*) R. Germani, G. Savelli, T. Romeo, N. Spreti, G. Cerichelli and C. A. Bunton, *Langmuir*, 1993, **9**, 55.

9 (*a*) R. Bacaloglu, C. A. Bunton, G. Cerichelli and F. Ortega, *J. Phys. Chem.*, 1989, **93**, 1490; (*b*) R. Bacaloglu, C. A. Bunton and F. Ortega, *J. Phys. Chem.*, 1989, **93**, 1497.

10 C. Bonan, R. Germani, P. P. Ponti, G. Savelli, G. Cerichelli, R. Bacaloglu and C. A. Bunton, *J. Phys. Chem.*, 1990, **94**, 533.

11 R. Bacaloglu, C. A. Bunton, G. Cerichelli and F. Ortega, *J. Phys. Chem.*, 1990, **94**, 5068.

12 (*a*) L. P. Hammett, *Physical Organic Chemistry*, McGraw-Hill, New York, 2nd edn., 1970, ch. 11; (*b*) J. Shorter, *Correlation Analysis of Organic Reactivity*, Research Studies Press, Chichester, 1982, chs. 3 and 5; (*c*) O. Exner, *Correlation Analysis of Chemical Data*, Plenum Press, London, 1988.

13 (*a*) K. A. Zachariasse, N. V. Phuc and B. Kozankiezi, *J. Phys. Chem.*, 1981, **85**, 2676; (*b*) C. Ramachandran, R. A. Pyter and P. Mukerjee, *J. Phys. Chem.*, 1982, **86**, 3198.

14 R. Germani, P. P. Ponti, G. Savelli, N. Spreti, C. A. Bunton and J. R. Moffatt, *J. Chem. Soc., Perkin Trans. 2*, 1989, 401.

15 T. J. Broxton, D. R. Fernando and J. E. Rowe, *J. Org. Chem.*, 1981, **46**, 3522.

16 (*a*) J. R. Hicks and V. C. Reinsborough, *Aust. J. Chem.*, 1982, **35**, 15; (*b*) C. Otero and E. Rodenas, *Can. J. Chem.*, 1985, **63**, 2892.

17 (*a*) S. O. Onyiuruka, C. J. Suckling and A. A. Wilson, *J. Chem. Soc., Perkin Trans. 2*, 1983, 1103; (*b*) M. T. Bianchi, G. Cerichelli, G. Mancini and F. Marinelli, *Tetrahedron Lett.*, 1984, 5205; (*c*) J. K. Sutter and C. N. Sukenik, *J. Org. Chem.*, 1982, **47**, 4174; (*d*) D. A. Jaeger and J. Wang, *Tetrahedron Lett.*, 1992, **33**, 6415; (*e*) C. Lapinte and P. Viout, *Tetrahedron Lett.*, 1972, 4221; 1973, 1113; (*f*) C. A. Bunton, A. A. Kamego and P. Ng, *J. Org. Chem.*, 1974, **39**, 3469; (*g*) D. A. Jager, M. W. Clennan and J. Jamrozik, *J. Am. Chem. Soc.*, 1990, **112**, 1171.

18 C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca, New York, 2nd edn., 1969, ch. 7.

19 G. Cerichelli, G. Mancini, L. Luchetti, G. Savelli and C. A. Bunton, *J. Phys. Org. Chem.*, 1991, **4**, 71.

20 (*a*) C. E. Coulthard, J. Marshall and F. L. Pyman, *J. Chem. Soc.*, 1930, 280; (*b*) L. Birckenbach and K. Meisenheimer, *Ber. Bunsenges. Phys. Chem.*, 1936, **69**, 723; (*c*) G. Cilento, *J. Am Chem. Soc.*, 1953, **75**, 3748.

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