Solvent and Micellar Effects upon the Cyclisation of *o*-3-Halopropyloxyphenoxide Ions

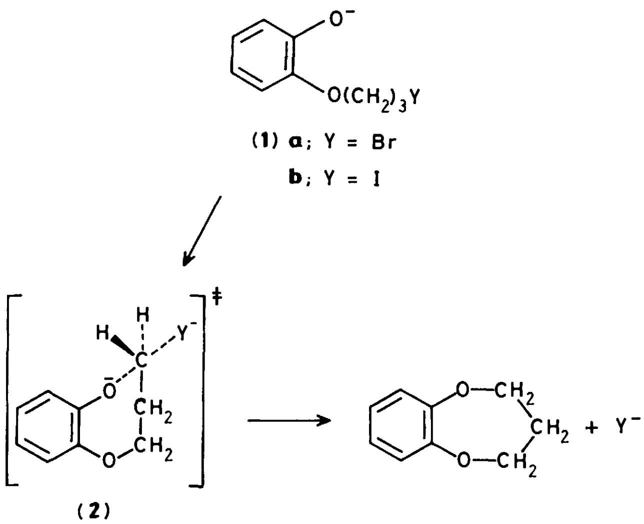
Giorgio Cerichelli,* Luciana Luchetti, Giovanna Mancini, and Maria Novella Muzzioli
Centro CNR di Studio sui Meccanismi di Reazione, Dipartimento di Chimica, Università La Sapienza, 00185 Roma, Italy
Raimondo Germani, Pier Paolo Ponti, Nicoletta Spreti, and Gianfranco Savelli*
Dipartimento di Chimica, Ingegneria Chimica e Materiali, Università di L'Aquila, 67100 L'Aquila, Italy
Clifford A. Bunton
Department of Chemistry, University of California, Santa Barbara, California 93106, USA

Rates of intramolecular cyclisations of *o*-(3-halopropyloxy)phenoxide ion [(**1a**, **b**), halogen = Br or I, respectively] increase with decreasing solvent polarity in the order H_2O < MeOH < EtOH < Pr^iOH < MeCN, except that reaction of (**1a**) is faster in H_2O than in MeOH, and in H_2O (**1a**) is more reactive than (**1b**). These effects depend upon the solvation of the oxide ion and the leaving halide ion in the transition state, and relative reactivities k^I/k^{Br} indicate the relative importance of these interactions. Micelles of CTAX [$C_{16}H_{33}NMe_3X$, X = Br, Cl, NO_3, OH, OTs, or $(SO_4)_{0.5}$] increase the rates by factors of *ca.* 2 for (**1a**) and by 4 for (**1b**), with little effect by the counter-ion. Rate enhancements and k^I/k^{Br} increase sharply in the sequence of surfactant head groups N^+Me_3 < N^+Et_3 < N^+Pr_3 < N^+Bu_3. Increasing the size of the n-alkyl group apparently decreases hydration of the aryloxide without destabilising the transition state. These micellar medium effects can be related to medium effects in intermolecular reactions in micelles.

Aqueous micelles can accelerate both spontaneous reactions and non-spontaneous bimolecular reactions.[1–4] They exert a medium effect on spontaneous reactions but they can accelerate, or inhibit, bimolecular reactions by bringing reactants together at the micellar surface, or by keeping them apart, and this concentration effect will be independent of medium effects upon the second-order rate constants at the micellar surface. Micellar effects upon many reactions of non-ionic substrates with hydrophilic ions have been treated quantitatively in terms of a pseudophase model in which micelles and water are treated as distinct regions.[2–4] The overall reaction rate then depends upon the concentrations of reactants in each region and the related second-order rate constants. The key problem is the estimation of the concentration of ionic reagent at the micellar surface, and in favourable cases ionic distribution between water and micelles can be measured directly, for example electrochemically or by fluorescence techniques.[5] In other cases, for example with OH^-, the distribution is calculated generally in terms of ion-exchange equations that describe interionic composition for the micellar surface. These treatments have been described in detail, and they successfully describe the dependence of rate on surfactant concentration for many reactions.[2–4,6,7]

For many ion–molecule reactions second-order rate constants at the micellar surface appear to be very similar to those in water, although for some unimolecular, spontaneous, reaction rate constants are very different in aqueous and micellar pseudophases. Estimations of second-order rate constants at micellar surfaces involve a variety of assumptions, and it is difficult to test them. So conclusions regarding second-order rate constants at micellar surfaces are suspect. A test reaction was, therefore, chosen in which concentration effects are absent but the transiton state of which is similar to that of a bimolecular ion–molecule reaction.

Cyclisations of *o*-3-halopropoxyphenoxide ion (**1a**, **b**) have transition states (**2**) the geometry of which at the reaction centre is that of an intermolecular S_N2 reaction (Scheme 1), but it is a first-, rather than a second- order process.[8,9] Therefore, the rate constant, for fully micellar-bound substrate, will depend only upon the medium effect of the micelle, whereas both concentration and medium effects control micellar rate enhancements of S_N2 reactions.



Scheme 1.

Cyclisations of *o*-(ω-haloalkoxy)phenoxide ions have been widely studied in non-micellar systems, especially with regard to the high reactivity of these compounds as given by the effective molarities (EM).[8,9] Solvent effects are very similar upon these and related intermolecular S_N2 reactions of aryloxide ions with alkyl halides, and have similar origins, *viz.* protic solvents slow the reaction by solvating the nucleophilic oxide ion.[10] Therefore, medium effects of micelles upon reactions of (**1**) should provide evidence for micellar medium effects on bimolecular, S_N2, reactions of hydrophilic anions.

A variety of surfactants was used and for some of them a wide

Table 1. Solvent effect upon cyclisation in the absence of surfactant.[a]

Solvent[a]	$k_{obs}/10^{-4}$ s^{-1} X = Br	I	$k^{\mathrm{I}}/k^{\mathrm{Br}}$
MeCN	107.00	320.00	3.03
Pr^{i}OH	15.00	22.00	1.47
EtOH	5.80	8.98	1.55
MeOH	1.02	1.58	1.56
H_2O	2.33	1.40	0.60

[a] At 25.0 °C in 97% organic solvent with KOH (0.1 cm^3; 0.3 mol dm^{-3}) in 3 cm^3 of reaction solution.

Table 2. Reaction in cationic micelles.[a]

[Surfactant]/ 10^{-3} mol dm^{-3}	CTABr	CTEABr	CTPABr	CTBABr
0.1	2.56(1.80)	2.72(2.61)	3.62(4.37)	5.24(22.5)
0.2	2.60(2.80)	(4.65)	6.17(9.04)	8.65(32.3)
0.4	—	—	9.47(16.3)	11.9(35.0)
0.5	3.80(5.00)	5.16(8.02)	—	—
0.6	3.80	—	11.0(20.3)	13.8(37.2)
1.0	4.02(5.00)	5.90(9.71)	11.9(23.3)	14.8(39.7)
3.0	4.02(5.04)	5.37(9.88)	18.8(25.1)	15.7(40.3)
4.0	4.10	6.02(9.98)	—	—
6.0	3.79(5.20)	6.24(10.1)	13.0(25.0)	16.5(41.2)
10.0	4.10(5.50)	6.01(9.79)	12.9(26.3)	16.8(41.0)
25.0	4.05(5.50)	—	—	—

[a] Values of $k_{obs}/10^{-4}$ s^{-1} at 25.0 °C for the reaction of the bromide (**1a**) in 0.01 mol dm^{-3} OH$^-$, values in parentheses are for the iodide (**1b**). In the absence of surfactant k_{obs} = 2.33 and 1.40 × 10^{-4} s^{-1} for reactions of (**1a**) and (**1b**), respectively.

Table 3. Effect of micellar head group.[a]

Surfactant	Substrate (**1a**)	(**1b**)	$k_M^{\mathrm{I}}/k_M^{\mathrm{Br}}$
CTABr	4.10(1.8)	5.50(3.9)	1.34
CTEABr	6.10(2.6)	10.0(7.1)	1.63
CTPABr	13.0(5.6)	26.0(18.6)	2.00
CTBABr	16.7(7.2)	41.0(29.0)	2.46

[a] Values of $k_M/10^{-4}$ s^{-1}, values in parentheses are k_M/k_W.

concentration range was examined to ensure that the substrates were fully micellar bound. The surfactants were hexadecyltrialkylammonium bromides (cetyltrialkylammonium bromides) ($C_{16}H_{33}NR_3Br$; CTABr, R = Me; CTEABr, R = Et; CTPABr, R = Pr; CTBABr, R = Bu) and CTAX, where X = Cl, NO_3, OH, OTs, $(SO_4)_{0.5}$.

Results

Reaction in the Absence of Surfactant.—Solvent effects are illustrated in Table 1. Reaction of the bromide substrate (**1a**) is faster than for the iodide (**1b**) in water, although alkyl iodides are generally more reactive than the bromides,[10] and the usual behaviour is seen in the other solvents. For the iodide (**1b**) k_{obs} increases in the expected sequence H_2O < MeOH < EtOH < Pr^{i}OH < MeCN, but the reaction of the bromide being slower in 97% MeOH than in H_2O was unexpected for this S_N2-like reaction.

Reactions in water are unaffected by dilute electrolyte or variations in concentrations of NaOH or KOH from 0.008–0.16 mol dm^{-3}, within experimental error.

Micellar Effects.—For both substrates k_{obs} increases monotonically with increasing concentration of the surfactant, $C_{16}H_{33}NR_3Br$, and becomes constant when the substrate is fully bound, but rate enhancements are very sensitive to the bulk of the head group (Tables 2 and 3). The first-order rate constants in water and micelles are designated k_W and k_M respectively, and superscripts Br and I are used to designate reaction of (**1a**) and (**1b**) respectively.

The iodide is consistently more reactive than the bromide, as for non-micellar reactions in organic solvents (Table 1), but for both reactions in hexadecyltrimethylammonium surfactants the rate constants, and in particular values of $k_M^{\mathrm{I}}/k_M^{\mathrm{Br}}$, are not very sensitive to the nature of the counter-ion (Tables 4–6) or to added Br$^-$ (Table 7). The small rate changes are probably due to differences in the surface packing of micellar head groups induced by the counter-ions, because micellar aggregation numbers and radii are affected by the counter-ions.[11] For both substrates the rate constants follow the sequence: SO_4^{2-} > Cl^- > Br^- > NO_3^-, and the rate constants for reaction of the bromide (**1a**) are similar in CTACl and CTAOH. Reaction of the bromide was also followed in CTAOTs, but more than 2 × 10^{-3} mol dm^{-3} CTAOTs could not be used, because the solutions become very viscous at greater concentrations. The rate constants in these conditions are slightly lower than those in CTABr (Table 4).

Aryloxide ions bind very strongly to cationic micelles with binding constants greater than 10^3 dm^3 mol^{-1} so that for micelles with low critical micelle concentrations, (cmc), substrates should be essentially fully bound in 10^{-2} mol dm^{-3} surfactant,[12] and rate–surfactant profiles fit this assumption. Rate constants for fully bound substrates change little with surfactant concentration and the small changes in k_M at high concentration of some of the surfactants are probably related to changes in micelle structure.[11] There are rate enhancements below the cmc in water[13] due to induced micellisation or reaction in submicellar aggregates.

Discussion

Micelles affect spontaneous cyclisations of *o*-(3-halopropyloxy)-phenoxide ions (**1a,b**) by a medium effect, although in bimolecular reactions of oxide and other nucleophilic ions micelles increase reactant concentrations at their surfaces and also exert a medium effect.[2–7] It is necessary, therefore, to consider, firstly, medium effects in reactions in the absence of surfactant.

Non-micellar Reactions.—Bimolecular reactions of nucleophilic anions with non-ionic substrates are typically speeded by a decrease in polarity and hydrogen-binding ability of the solvent.[10,14] Stabilisation of the nucleophilic anion by hydrogen binding plays a major role, and these anionic reactions are much faster in polar aprotic solvents than in protic solvents of similar polarity, and cyclisations of (**1a, b**) and similar substrates are very much faster in moist Me_2SO than in aqueous EtOH.[8,9] Interpretation of rates of lyate ion reactions in aqueous alcohols are complicated by the hydroxide–alkoxide ion equilibrium, because the addition of an alcohol to water changes the polarity and medium effects of the solvent and also replaces OH$^-$ by the more nucleophilic alkoxide ion. This complication is absent in the cyclisation of (**1a, b**), and similar substrates, where the nucleophile is always the aryloxide ion, and, as expected, reactivity of the iodide (**1b**) increases in the sequence H_2O < MeOH < EtOH < Pr^{i}OH < MeCN (Table 1) and reaction is fastest in 97% MeCN. Reaction of the bromide (**1a**) in H_2O is faster than in 97% MeOH, and H_2O the bromide is more reactive than the iodide.

These results are probably due to electrophilic assistance by hydrogen bonding to the leaving bromide ion which more than offsets deactivation by hydrogen bonding to the aryloxide ion in

Table 4. Effect of counter-ion on the reaction of the bromo substrate (**1a**) in micelles.

	X						
[CTAX]/10^{-3} mol dm^{-3}	Cl	Br	NO_3	OTos	OH	OH[b]	$(SO_4)_{0.5}$
0.05		2.38		2.50			
0.10	2.40	2.50	2.35	2.51			
0.15	2.42	2.40	2.41				2.43
0.25	3.10	2.80 (2.71)		2.87			2.94
0.50	3.48	3.80 (2.97)	3.30	3.26			4.03
0.75		3.80	3.67	3.43			
1.0	4.03	3.98 (3.30)	3.81	3.45	4.12	3.10	4.08
2.0		4.00		3.67			4.53
2.5	4.12	(3.72)	3.63			3.30	
5.0	4.25	4.10 (4.22)	3.47		4.01	3.46	4.58
7.5	4.30	4.00 (4.22)	3.40			3.62	
10		4.10 (4.43)	3.40		4.04	3.63	4.58
20					4.16	3.82	4.80
25	4.42	4.05 (4.47)	3.28				
50	4.40	4.10			4.33	4.13	
100					4.48	4.57	

[a] Values of $k_{obs}/10^{-4}$ s^{-1} at 25.0 °C and 0.01 mol dm^{-3} OH^- unless specified; values in parentheses are with added 0.1 mol dm^{-3} NaBr, in water $k_{obs} = 2.33 \times 10^{-4}$ s^{-1}. [b] No added OH^-.

Table 5. Effect of counter-ion on the reaction of iodo substrate (**1b**) in micelles.

	X			
[CTAX]/10^{-3} mol dm^{-3}	Cl	Br	NO_3	$(SO_4)_{0.5}$
0.05		1.50		
0.10	1.65	1.80	1.83	
0.15	2.00	2.20	2.00	2.12
0.25	4.10	3.40	3.23	3.60
0.50	4.30	5.00	3.48	4.60
0.75	4.70	5.00	3.38	
1.0	4.98	5.00	4.32	5.40
2.5	5.20	5.00	4.58	6.00
5.0	5.40	5.00	4.62	6.20
7.5	5.50	5.20	4.50	
10	5.40	5.50	4.70	6.47
20				6.47
25	5.60	5.50	4.70	
50	5.70	5.50		

[a] Values of $k_{obs}/10^{-4}$ s^{-1} at 25.0 °C and 0.01 mol dm^{-3} OH^-, in water $k_{obs} = 1.40 \times 10^{-4}$ s^{-1}.

Table 6. Effect of counter-ions on micellar reactions.[a]

	$k_M/10^{-4}$ s^{-1}		
Surfactant	X = Br	Cl	k_M^I/k_M^{Br}
CTABr	4.1	5.5	1.3
CTACl	4.35	5.55	1.3
$CTANO_3$	3.4	4.7	1.4
$(CTA)SO_{0.5}$	4.8	6.5	1.35
CTAOH[b]	4.5		
CTAOTos	*ca.* 3.7[c]		

[a] At 25.0 °C with 10^{-2} mol dm^{-3} KOH and 10^{-2} mol dm^{-3} surfactant. [b] In 0.1 mol dm^{-3} surfactant. [c] In 2×10^{-3} mol dm^{-3} surfactant.

Table 7. Salt effects on the micellar reaction of the bromide (**1a**).[a]

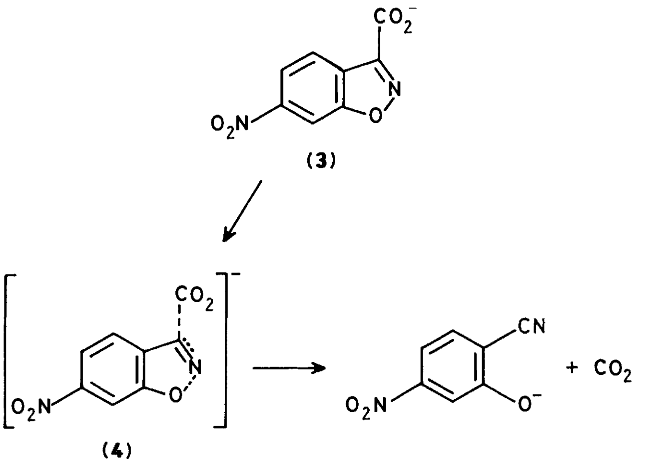
[Surfactant]/mol dm^{-3}	$k_{obs}/10^{-4}$ s^{-1}
0.025	4.39
0.035	4.41
0.040	4.44
0.045	4.42
0.046	3.57[b]
0.046	3.56[c]

[a] At 25.0 °C with CTABr + 0.1 mol dm^{-3} NaBr + 0.01 mol dm^{-3} NaOH unless specified, with no added salt $k_{obs} = 4.1 \times 10^{-4}$ s^{-1}. [b] In $CTANO_3$ with 0.088 mol dm^{-3} $NaNO_3$, in the absence of salt $k_{obs} = 3.4 \times 10^{-4}$ s^{-1}. [c] In $CTANO_3$ with 0.17 mol dm^{-3} $NaNO_3$.

the initial state. This assistance will be smaller for the bulkier leaving iodide ion, and here solvent effects are 'normal'.[10,14]

Micellar Effects.—Our results on the cyclisation of *o*-(3-halopropyloxy)phenoxide ions (**1**) show that rate constants in hexadecyltrimethylammonium surfactants are larger than those in water by a factor of approximately two for the bromide (**1a**) and less than four for the iodide (**1b**) (Tables 2, 4, and 5). These rate enhancements are qualitatively similar to those in a hypothetical solvent, the polarity of which is intermediate between those of MeOH and EtOH (Table 1), and values of k_M^I/k_M^{Br} *ca.* 1.4 in micellar pseudophases of CTA^+ and $CTEA^+$ are very similar to those in alcohols (Table 1). These conclusions are consistent with spectrometric estimates of apparent dielectric constant, or effective polarity, at micellar surfaces that indicate that the values of these properties are similar to those of MeOH or EtOH.[2,15] However, values of k_M^I/k_M^{Br} in CTPABr and CTBABr (Tables 2 and 3) are larger than those in the alcohols and reflect the apolar nature of the micellar surface with these bulky head groups which favours reaction of the iodide relative to the bromide.

Values of second-order rate constants of ion–molecule reactions at the surfaces of ionic micelles of CTA^+ are similar to, but generally slightly smaller than, those in water, provided that concentration effects are factored out.[2–4] These reactions are, in effect, intramolecular ion–molecule reactions, and the similarity of rate constants in micellar and aqueous pseudophases suggests that rate constants of mechanistically similar S_N2 reactions should also be similar in the two pseudophases. This was concluded from quantitative analyses of micellar rate effects, even though estimation of second-order rate constants in micellar pseudophases depends directly upon assumed volumes of the reaction region at the micellar surface.[2–4] A constant value for this volume is generally assumed, although it may



Scheme 2.

depend to some extent upon the surfactant and the nature of the region.[16]

Values of k_M/k_W are in the range of 2–4 for reactions in CTA^+ micelles, with little dependence upon the counter-ion (Tables 4–6), but they increase markedly with increasing bulk of the cationic head group from N^+Me_3 to N^+Bu_3 and the increase is much larger for reaction of the iodide (**1b**) than of the bromide (**1a**) (Table 3).

The micelle provides a reaction medium of lower polarity than water,[15] and the polarity should follow the head group sequence Me > Et > Pr^n > Bu. Analogies between the medium properties of micellar surface and homogeneous solvents are useful, but should not be taken too far because the micellar surface is not a continuous medium, due to the presence of ionic head groups and counter-ions, and the possible intercalation of water between the surfactant head groups and adjacent regions of the hexadecyl group.

Solvent effects on the reaction rate can be rationalised by assuming that hydroxy groups reduce the reactivity of the oxide ion by hydrogen bonding,[8,9] and increase reactivity by hydrogen bonding to the leaving halide ion. This increase is more important for the bromide than the iodide substrate. The micellar head groups can control reactivity by excluding water from the surface, which will increase reactivity of the oxide ion, but decrease hydration of the leaving halide ion. However, cationic micellar head groups interact readily with Br^- and even more strongly with I^-,[2,5] so that they should provide electrophilic assistance to reaction. These interactions involve dispersive, as well as coulombic, interactions so that a Bu_3N^+ group, for example, should interact more strongly with a forming iodide ion than with a bromide ion in reactions of (**1a, b**). These considerations neglect possible micellar effects upon substrate conformations, based on reactivities in non-micellar media and the situation may be different for reactions of substrates that have medium or long methylene chains.[8,9]

Values of fractional ionisation, α, for micelles of $R'N^+R_3$ (Cl^-, Br^-), where R = $C_{14}H_{29}$ or $C_{16}H_{33}$, increase with increasing size of R in the sequence Me < Et < Pr^n < Bu, for both chloride and bromide surfactants,[17] and the interaction of Br^- with the head groups decreases in going from Me to Bu, based on the evidence of n.m.r. data.[18] The nucleophilicities of Cl^- and Br^- towards methyl naphthalene-2-sulphonate increase as the head group size is increased from N^+Me_3 to N^+Bu_3.[18] The increases are smaller than those for cyclisation but they appear to have similar origins, even though we are comparing inter- and intra-molecular reactions.

Although values of k_M for cyclisation are only slightly affected by changes in the counter-ion (Tables 4–7), they increase slightly with its increasing hydrophilicity by decreasing the ability of water molecules at the micellar surface to deactivate the oxide ion of the substrate. Micellar rate increases in these intramolecular S_N2-like reactions are much smaller than those for spontaneous dephosphorylation and decarboxylation.[2b,19] Rate enhancements of decarboxylation of 6-nitrobenzisoxazole-3-carboxylate ion (**3**) are in the range 10^2–10^3.

Despite the large differences in the micellar rate enhancements in the two systems, similar interactions are involved. Decreases in hydrogen bonding to the initial states (**1**) and (**3**) speed reaction both in the presence of micelles and in different solvents.[8,9,20]

The charge-delocalised transition state (**4**) (Scheme 2) should be effectively stabilised by interaction with cationic head groups that interact most strongly with anions that have dispersed, rather than localised, charge.[2] The charge in the transition state (**2**) will be localised largely on oxygen and halogen, based on an analogy with intermolecular S_N2 reactions,[10,14] and these centres can readily form hydrogen bonds with protic solvents. Therefore, the reaction of (**1**) stabilised by interaction with micellar head groups will be partially offset by compensating changes in hydrogen bonding at oxide and leaving-halide centres. Solvent effects, upon cyclisation of (**1**), are smaller than upon decarboxylation of (**3**) (Table 1 and refs. 8, 9, and 20).

Our results are consistent with the generalisation that rate enhancements of anion–molecule reactions by micelles with trimethylammonium head groups are due largely to a concentration of reagents at the micellar surface.[2–4,6,7] The increasing micellar rate enhancements with increasing bulk of the head group (Tables 2 and 3) suggest that this generalisation will be less satisfactory for bimolecular reactions in micellised CTBAX, for example. The micellar medium effect should depend upon the extent to which charged centres in the initial and transition states interact with water by hydrogen bonding and cationic head groups by coulombic and dispersive forces, but we predict that second-order rate constants of bimolecular anionic reactions at micellar surfaces will tend to be higher than in water when the cationic surfactant has bulky trialkylammonium head groups, as for attack of Br^- on methyl naphthalene-2-sulphonate in CTABr, CTEABr, CTPABr, and CTBABr.[18]

Experimental

Materials.—The preparation of the bromide (**1a**) has been described,[8] and the iodide (**1b**) was prepared from catechol and 1,3-di-iodopropane following the general procedure of Illuminati *et al.*[8] by shaking the reagents under heterogeneous conditions in aqueous NaOH. The crude product was dried and although it had the predicted mass number by high resolution mass spectrometry it was shown to contain *ca.* 10% of the cyclisation product by g.l.c. analysis. Crystallisation from a variety of aprotic solvents did not eliminate the cyclic ether, probably because cyclisation is fast in aprotic media. Crude dried material was therefore used in the kinetics measurements which were unaffected by the presence of the product. The surfactants were prepared by standard methods as described,[2,18] and reactions were followed in redistilled CO_2-free H_2O.

Kinetics.—Reactions were followed spectrophotometrically at 290 nm and 25.0 °C in HP diode array or Varian 210 and 219 spectrometers. The substrate concentration was generally 10^{-4} mol dm^{-3} and it was added to the reaction solution in EtOH or MeCN so that the final solution contained 0.1% organic solvent in addition to the specified solvent. 97 vol% organic solvent was used in the absence of surfactant because KOH is insoluble in dry MeCN.

Reactions were clearly first order up to 95% under all conditions and intermolecular reactions could be neglected. The rate constants were unaffected, within experimental error, by changes in [substrate] or changes in [OH^-] from 8×10^{-3} to 0.16 mol dm^{-3} NaOH or KOH, so that there was no reaction with OH^-. A few experiments were carried out with [substrate] up to 4×10^{-4} mol dm^{-3} without effect on the first-order rate constants, so it can be assumed that attack of aryloxide ion can be neglected.

Acknowledgements

Support of this work by CNR (Roma), the Ministero della Pubblica Istruzione and the National Science Foundation (Chemical Dynamics Program) is gratefully acknowledged.

References

1 J. H. Fendler, 'Membrane Mimetic Chemistry,' Wiley Interscience, New York, 1982.
2 (*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*) C. A. Bunton and G. Savelli, *Adv. Phys. Org. Chem.*, 1986, **22**, 213.
3 K. Martinek, A. K. Yatsimirski, A. V. Levashov, and I. V. Berezin, in 'Micellization, Solubilization and Microemulsions,' ed. K. L. Mittal, Plenum Press, New York, vol. 2, 1977, p. 489.
4 F. H. Quina and H. Chaimovich, *J. Phys. Chem.*, 1979, **83**, 1844.
5 (*a*) J. W. Larsen and B. Tepley, *J. Colloid Interface Sci.*, 1974, **49**, 113; (*b*) C. A. Bunton, K. Ohmenzetter, and L. Sepulveda, *J. Phys. Chem.*, 1977, **81**, 2000; (*c*) E. Lissi, E. B. Abuin, L. Sepulveda, and F. H. Quina, *ibid.*, 1984, **88**, 81.
6 E. Rodenas and S. Vera, *J. Phys. Chem.*, 1985, **89**, 513.
7 (*a*) C. A. Bunton and J. R. Moffatt, *J. Phys. Chem.*, 1986, **90**, 538; 1988, **92**, 2896; (*b*) E. Rodenas and F. Ortega, *ibid.*, 1987, **91**, 837.
8 (*a*) G. Illuminati, L. Mandolini, and B. Masci, *J. Am. Chem. Soc.*, 1977, **99**, 630; (*b*) A. Dalla Cort, G. Illuminati, L. Mandolini, and B. Masci, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1774.
9 L. Mandolini, *Adv. Phys. Org. Chem.*, 1986, **22**, 1.
10 T. H. Lowry and K. S. Richardson, 'Mechanism and Theory in Organic Chemistry,' Harper and Row, New York, 3rd edn., 1987, ch. 4.
11 (*a*) S. Ikeda, S. Hayashi, and T. Imae, *J. Phys. Chem.*, 1981, **85**, 106; (*b*) H. Hoffman, G. Platz, H. Rehage, and W. Schorr, *Ber. Bunsenges. Phys. Chem.*, 1981, **85**, 877; (*c*) D. C. McKenzie, C. A. Bunton, D. F. Nicoli, and G. Savelli, *J. Phys. Chem.*, 1987, **91**, 5709.
12 C. A. Bunton and L. Sepulveda, *Isr. J. Chem.*, 1979, **18**, 298.
13 P. Mukerjee and K. J. Mysels, 'Critical Micelle Concentrations of Aqueous Surfactant Systems,' National Bureau of Standards, Washington, DC, 1970.
14 C. K. Ingold, 'Structure and Mechanism in Organic Chemistry,' Cornell University Press, Ithaca, NY, 1969, ch. 7.
15 (*a*) E. H. Cordes and C. Gitler, *Progr. Bio-org. Chem.*, 1973, **2**, 1; (*b*) C. Ramachandran, R. A. Pyter, and P. Mukerjee, *J. Phys. Chem.*, 1982, **86**, 3198.
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 R. Zana, *J. Colloid Interface Sci.*, 1980, **78**, 330.
18 R. Bacaloglu, C. A. Bunton, G. Cerichelli, and F. Ortega, *J. Phys. Chem.*, submitted.
19 (*a*) C. A. Bunton, M. J. Minch, J. Hidalgo, and L. Sepulveda, *J. Am. Chem. Soc.*, 1973, **95**, 3262; (*b*) R. Germani, P. P. Ponti, G. Savelli, N. Spreti, A. Cipiciani, B. Cerichelli, and C. A. Bunton, *J. Chem. Soc., Perkin Trans. 2*, in press.
20 D. S. Kemp and K. Paul, *J. Am. Chem. Soc.*, 1975, **97**, 7305.

Received 20*th March* 1989; *Paper* 8/03669A