Nucleophilic Aromatic Substitution in Solutions of Cationic Bolaform Surfactants

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Reactions of OH^- with 2,4-dinitro-1-chloro-benzene and -naphthalene have been examined in solutions of the following bolaform surfactants: alkane-α,ω-bis(trimethylammonium bromide), alkane = docosane, hexadecane, and dodecane, [bolaform(22)Br, bolaform(16)Br, and bolaform(12)Br], bolaform(22)OH, and bolaform(16)OH. Rate effects of bolaform(22)Br and OH^- were analysed quantitatively in terms of distribution of reactants between water and micelles and second-order rate constants at the micellar surfaces were very similar to those found with normal hexadecyltrimethylammonium micelles. Rate effects were much smaller with bolaform(16)Br and OH^- but were typical of micellar rate enhancements, and bolaform (12)Br had even smaller effects.

So-called bolaform electrolytes which have ionic head groups at the α- and ω-position of an alkyl chain can form micelles provided that the chain is long.[1,2] For example, docosane-1,22-bis(trimethylammonium bromide) [bolaform(22)Br] (**1a**),

$$X^- \ Me_3\overset{+}{N}(CH_2)_{22}\overset{+}{N}Me_3 \ X^-$$

(**1**)
a; X = Br
b; X = Cl
c; X = OH

appears to form normal micelles in water.[1c] However, if the chain is short, *e.g.*, hexadecane or dodecane, there is surface activity, but less clear-cut evidence for normal micellization.[1a,b,2]

To data there has been little work on effects of these electrolytes on reaction rates and equilibria. Menger and Wrenn examined ester saponification in the relatively short-chain bolaform electrolytes (**2a,b**) and found rate enhancements to be

$$Br^- \ Me_3\overset{+}{N}(CH_2)_n\overset{+}{N}Me_3 \ Br^-$$

(**2**)
a; *n* = 4
b; *n* = 12
c; *n* = 16

smaller than those expected for solutions of cationic micelles.[2]

We have examined the effects of the bolaform electrolytes (**1a**—**c**) on reactions of OH^- with 2,4-dinitro-1-chloro-benzene and -naphthalene (DNCB and DNCN, respectively) and compared these rate effects with those of cetyltrimethylammonium surfactants which form normal micelles in water.[3-5] The rate effects were treated quantitatively using the pseudophase ion-exchange model.[6]

Experimental

Materials.—Docosane-1,22-bis(trimethylammonium bromide) [bolaform(22)Br] was prepared from docosa-1,21-diene by its conversion into the 1,22-dibromide with HBr in toluene at −5 °C.[7] The dibromide was recrystallized (EtOH) and had m.p. 72—73 °C (lit.,[7] 72—73 °C), δ(CCl_4) 3.30 (4 H, t), 1.80 (4 H, m), and 1.25 (36 H, s), *m/e* 468 (Found: C, 56.3; H, 9.45; Br, 34.1. Calc. for $C_{22}H_{44}Br_2$: C, 56.4; H, 9.5; Br, 34.1%). The dibromide was quaternized with Me_3N in EtOH under reflux for 6 h.[2] It was recrystallized from MeCN–Et_2O (Found: C, 57.1; H, 10.7; N, 4.7; Br, 27.3. Calc. for $C_{28}H_{62}Br_2N_2$: C, 57.3; H, 10.65; N, 4.8; Br, 27.2%). The critical micelle concentration (c.m.c.) was 2.8 × 10^{-3}M by surface tension at 25 °C and was *ca.* 6 × 10^{-4}M in 0.02M-NaBr.

Bolaform(22)Br was converted into the sulphate by treatment with Ag_2SO_4 in MeOH with ultrasonication to break up solids.[4] After removal of solids the solution was concentrated and the sulphate precipitated on addition of Et_2O. It had c.m.c. 1.9 × 10^{-3}M at 25 °C by surface tension with no minimum.

The sulphate was converted into the hydroxide by treatment with an equivalent amount of $Ba(OH)_2$ in absence of CO_2, and $BaSO_4$ was removed by extensive centrifugation.[4] The solution was tested for Ba^{2+} and SO_4^{2-}, which were absent. The c.m.c. was 1.03 × 10^{-3}M by surface tension.

Bolaform(22)Br was converted into the chloride using Amberlite IRA-400-Cl in MeOH. The resin was washed extensively with distilled H_2O and then with MeOH, much of which was removed under reduced pressure. The initial solution of bolaform(22)Cl in MeOH was passed through a small column of silica gel to remove any organic contaminants. Bolaform(22)Cl was precipitated from MeOH by Et_2O. The solid was tested for bromide ion, which was absent (Found: Cl, 14.2. Calc. for $C_{28}H_{62}Cl_2N_2$: 14.2%). The c.m.c. was 3.3 × 10^{-3}M by surface tension.

Hexadecane-1,16-bis(trimethylammonium bromide) [bolaform(16)Br] was prepared *via* the dibromide.[1b] The 1,16-diol was treated with PBr_3 at 100—110 °C for 4 days.[8] The mixture was added to H_2O and the dibromide was extracted with Et_2O, washed, H_2O, $NaHCO_3$, and dried (Na_2SO_4), and treated with silica gel. The solid was recrystallized and had m.p. 55—56 °C (lit.,[8] 56—57 °C), and after hydrolysis it was titrated quantitatively for Br. It was quaternized as described for bolaform(22)Br (Found: C, 52.1; H, 10.4; N, 5.45; Br, 31.6. Calc for $C_{22}H_{50}Br_2N_2$: C, 52.5; H, 10.0; N, 5.6; Br, 31.8%). The c.m.c. was 3.1 × 10^{-3}M determined by surface tension, with no minimum. However, a plot of conductivity against concentration gave an ill-defined break at *ca.* 10^{-2}M and another break at *ca.* 4 × 10^{-2}M. This latter value is close to the c.m.c. of 4.6 × 10^{-2}M reported by Yiv and Zana, estimated conductimetrically.[1b]

Bolaform(16)OH was prepared from the bromide by the method described for bolaform(22)OH. The solution contained no Ba^{2+} or SO_4^{2-}.

Dodecane-1,12-bis(trimethylammonium bromide) [bolaform(12)Br] was prepared by quaternizing the 1,12-dibromide with Me_3N in MeOH.[1a] It was purified by recrystallization from EtOH–Et_2O and had m.p. 229—230 °C (Found: C, 48.5; H, 9.6;

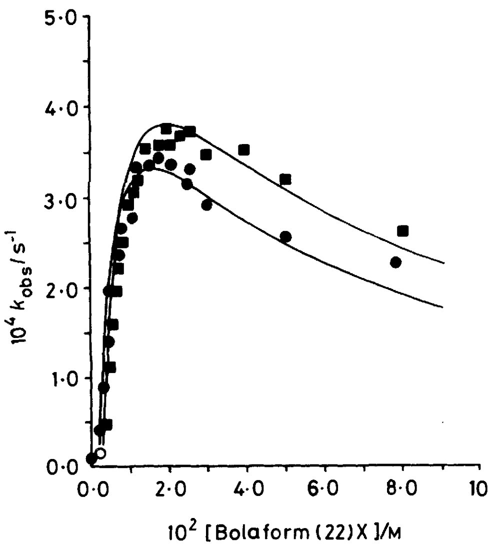

Figure 1. Reaction of DNCB, 0.05M-[$\mathrm{OH_T^-}$]: (●) in (**1a**); (■) in (**1b**)

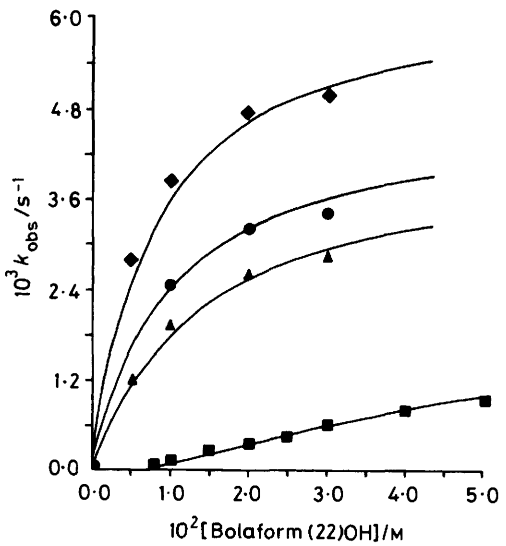

Figure 3. Reaction of DNCB in (**1c**): (■) no NaOH; (▲) 0.5M-[$\mathrm{OH_T^-}$]; (●) 0.66M-[$\mathrm{OH_T^-}$]; (◆) 1.0M-[$\mathrm{OH_T^-}$]

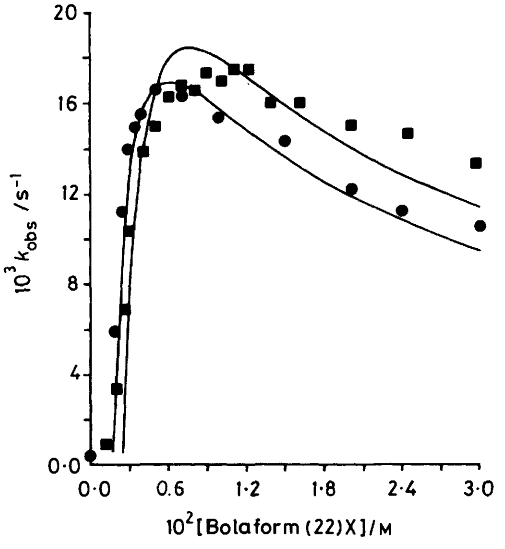

Figure 2. Reaction of DNCN, 0.05M-[$\mathrm{OH_T^-}$]: (●) in (**1a**); (■) in (**1b**)

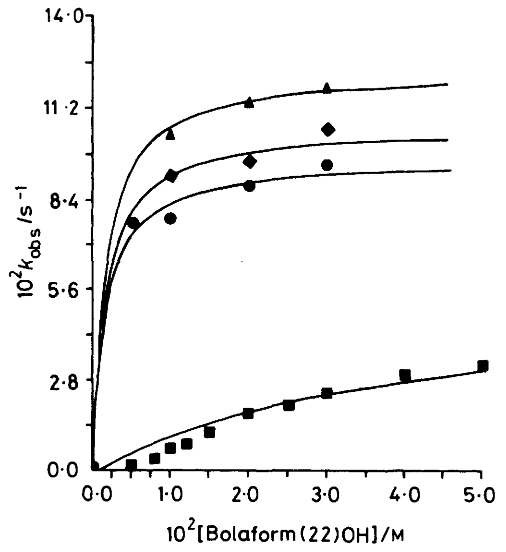

Figure 4. Reaction of DNCN in (**1c**): (■) no NaOH; (●) 0.5M-[$\mathrm{OH_T^-}$]; (◆) 0.66M-[$\mathrm{OH_T^-}$]; (▲) 1.0M-[$\mathrm{OH_T^-}$]

N, 6.2; Br, 35.4. Calc. for $C_{18}H_{42}Br_2N_2$: C, 48.4; H, 9.5; N, 6.3; Br, 35.8%). It was converted into the hydroxide form as described for the other materials.

Purification of the other materials has been described.[3,4]

Kinetics.—Reactions were followed spectrophotometrically at 25.0 °C using CO_2-free distilled H_2O and *ca.* 10^{-5}M-substrate.[3,4]

Results and Discussion

Rate Effects.—The variations of k_{obs} with concentrations of (**1a,b**) are shown in Figures 1 and 2 for reactions of DNCB and DNCN, respectively. Rates are enhanced by factors of *ca.* 50 over those in water, with the chloride (**1b**) being slightly more effective than the bromide (**1a**). (Second-order rate constants in water at 25.0 °C are 1.4×10^{-4} and 6.4×10^{-3} l mol^{-1} s^{-1} for reactions of DNCB and DNCN respectively).[3,4] The rate enhancements and the effects of the halide counterions are very similar to those found with micelles of single-chain surfactants,[3-5] and are consistent with (**1a,b**) forming aggregates whose surfaces are similar to those of normal micelles.

The halide ions can be replaced by OH^-, which becomes the only anion in solution. There is then no interionic competition, and values of k_{obs} increase with increasing [(**1c**)] even under conditions under which DNCN should be extensively bound (Figures 3 and 4). However, addition of OH^- increases k_{obs}, and at high OH^- it tends to level off with increasing [(**1c**)]. This behaviour is very similar to that for reactions in CTAOH and similar reactive-ion surfactants.[4,9]

Rate enhancements by bolaform(22)Cl, Br at the maxima are, for DNCB; Cl, 54; Br, 49; and in CTACl and CTABr are respectively 102 and 63.[5] Corresponding enhancements for DNCN are, for bolaform(22)Cl and Br, 54 and 52, respectively.

A few experiments were carried out on reactions in solutions of the hexadecane derivative [bolaform(16)OH] but rate

Table 1. Reactions in bolaform(16)OH[a]

	Substrate	
[Surfactant]/M	DNCB	DNCN
0.06	0.40 (2.43)	18 (119)
0.09	1.09 (4.15)	79 (246)
0.12	2.23 (6.23)	131 (299)
0.17		220

[a] Values of $10^4k_{obs}/s^{-1}$ at 25.0 °C, values in parentheses are with $[OH_T^-]$ 0.5M.

Table 2. Reactions in bolaform(16)Br[a]

	Substrate	
[Surfactant]/M	DNCB	DNCN
	0.07	3.2
0.03	0.11	18.7
0.04		21.9
0.05		23.5
0.06	0.35	24.1
0.07	0.37	23.5
0.08		23.6
0.10	0.55	21.1
0.12		21.6
0.16	0.62	19.0
0.18	0.62	
0.20		17.6
0.24	0.55	
0.25		17.9

[a] Values of $10^4k_{obs}/s^{-1}$ at 25.0 °C, with 0.05M-NaOH.

enhancements were small, and were observed only at high concentrations of the bolaform (Table 1). However, with (**2c**), values of k_{obs} went through maxima with increasing [(**2c**)] (Table 2). Such maxima are typical of micellar-enhanced reactions and are consistent with the pseudophase, ion-exchange model which postulates competition between reactive and inert ions for a micelle.[6]

We followed some reactions in solutions of bolaform(12)Br (**2b**) but relatively high surfactant had to be used and the rate enhancements were very small. The major problem, which led to the abandonment of these experiments, was formation of precipitates in the course of reaction. These precipitates did not form in the absence of NaOH and we assume that OH^- was attacking the bolaform and giving insoluble elimination or substitution products. These products did not form with the larger chain bolaforms, nor were they observed with other cationic surfactants in NaOH. It may be that with bolaform(12) the head groups come sufficiently close for enough time for attack of OH^- upon one of them to be assisted.[1b,c] Menger and Wrenn do not mention this problem,[2] but the pH of 12 of their solutions was lower than that of ours.

Kinetic Analysis.—The ion-exchange, pseudophase model was used.[6] Despite its shortcomings it fits a great deal of data.[10,11]

The first-order rate constant is given by equation (1) where

$$k_{obs} = \frac{k_W[OH^-] + k_M K_s m^s_{OH}[D_n]}{1 + K_s[D_n]} \qquad (1)$$

D_n is micellized surfactant,[12] K_s is the substrate binding constant, k_W l mol^{-1} s^{-1} the second-order rate constant, and k_M s^{-1} that in micelles.[4–6]

The usual equations[4–6] have to be modified for a bolaform surfactant and equation (2) is obtained where K_X^{OH} is the ion-exchange parameter and $m^s_{OH} = [OH_M^-]/2[D_n]$.[13–15]

$$(m^s_{OH})^2 + m^s_{OH}\left(\frac{[OH_T^-] + K_X^{OH}[X_T^-]}{2(K_X^{OH} - 1)[D_n]} - (1 - \alpha/2)\right) - \frac{[OH_T^-](1 - \alpha/2)}{2(K_X^{OH} - 1)[D_n]} = 0 \qquad (2)$$

Fitting of the data is discussed in ref. 5.

A major question is that of the appropriate value of the fractional ionization, α. Zana and his co-workers estimated α 0.38 for bolaform(22)Br from electrochemical data.[1c] A value of 0.40 has been estimated from dynamic light scattering of solutions of bolaform(22)Br + NaBr,[16] and similar values have been calculated from small-angle neutron scattering data in D_2O.[17] For bolaform(22)Cl α is 0.54.[16]

We did not attempt to fit the kinetic data for reactions in the C-12 or C-16 bolaforms because although these materials are surface active and aggregate, the aggregates are probably smaller than normal micelles, so that ion binding at the surface will be very different.

Reaction in Absence of Inert Counterion.—The binding of hydrophilic counterions to micelles of CTAOH or CTAF, for example, can be described by the mass-action-like equation (3),[4]

$$K'_{OH} = [OH_M^-]/[OH_W^-](2[D_n] - [OH_M^-]) \qquad (3)$$

which is written in terms of interaction with either of the two ionic head groups of a bolaform surfactant. Equations (1) and (2) can be combined, and the data fitted by computer simulation. Assumptions involved in derivation of these equations are discussed in the accompanying paper,[5] and the fits are shown in Figures 1—4.

Surface Tension of Bolaform(22) Surfactants.—Plots of surface tension against log [surfactant] were normal in that with increasing [surfactant] they were linearly descending to a break-point typical of micellization and at higher [surfactant] surface tension was constant.[18]

The c.m.c. of bolaform(22)Br of 2 × 10^{-3}M agrees well with values determined electrochemically by Zana *et al.*[1c] The values for the chloride and sulphate of 3.3 × 10^{-3} and 1.9 × 10^{-3}M, respectively, are consistent with the value for the bromide. However, the break point at 1.03 × 10^{-3}M for bolaform(22)OH would correspond to an unusually low c.m.c., because for single-chain surfactants hydroxides do not have lower c.m.c. than the chlorides or bromides.[4,18,19] If anything, values are higher, although for CTAOH the significance of a c.m.c. is not obvious.[4] Menger and Wrenn discussed the surface activity of bolaform surfactants on the assumption that the chain was bent, which allowed both head groups to enter the water with the chain in the air.[2] If this is the case surface activity, and therefore effects on surface tension, may depend upon the nature of the counterion, which if it is bromide may interact readily with the head groups, whereas there should be little interaction with a very hydrophilic counterion such as hydroxide.

It is understandable that surface tension and electrochemistry sometimes appear to give different values of the c.m.c. Surface tension senses coverage of the water surface by monomeric surfactant, whereas electrochemistry senses any ionic species in the water that include not only monomeric surfactant but also small *n*-mers which do not readily bind hydrophilic counterions. Thus CTAOH shows normal surface-tension be-

Table 3. Fitting parameters in bolaform(22) micelles[a]

Substrate	X	$[OH_T^-]$/M	K_s/l mol^{-1}	10^3k_M/s^{-1}
DNCB	Cl	0.05	55	4.9
DNCB	Br	0.05	65	5.0
DNCB	OH		40	4.0
DNCB	OH	0.50	70	4.8
DNCB	OH	0.66	100	5.2
DNCB	OH	1.00	130	6.7
DNCN	Cl	0.05	450	100
DNCN	Br	0.05	500	110
DNCN	OH		600	83
DNCN	OH	0.50	600	107
DNCN	OH	0.66	600	115
DNCN	OH	1.00	600	130

[a] Fitted taking the following parameters: α 0.54 and 0.40 for X = Cl and Br, respectively; K_X^{OH} = 8 and 17 for X = Cl and Br respectively; K'_{OH} = 10 l mol^{-1} for X = OH; c.m.c. 2.7 and 1.8 × 10^{-3}M for X = Cl and Br respectively, and c.m.c. 7 × 10^{-3}M for X = OH without added NaOH and 0 with added NaOH.

Table 4. Comparison of rate constants in water and micelles[a]

Substrate	Reaction medium	$10^3k_2^m$/l mol^{-1} s^{-1}	k_2^m/k_W
DNCB	Bolaform(22)Cl + OH^-	0.7	5.0
DNCB	Bolaform(22)Br + OH^-	0.7	5.0
DNCB	Bolaform(22)OH	0.6	4.1
DNCB	Bolaform(22)OH + OH^-	0.7	4.9
DNCB	CTACl + OH^-	0.55[b]	3.9
DNCB	CTABr + OH^-	0.49[b]	3.5
DNCB	CTAOH	0.7[c]	5.0
DNCB	CTAOH + OH^-	1.0[c]	7.0
DNCN	Bolaform(22)Cl + OH^-	14	2.2
DNCN	Bolaform(22)Br + OH^-	16	2.5
DNCN	Bolaform(22)OH	12	1.9
DNCN	Bolaform(22)OH + OH^-	15	2.4
DNCN	CTACl + OH^-	14.7[b]	2.3
DNCN	CTABr + OH^-	12.0[b]	1.9
DNCN	CTAOH	15[c]	2.3
DNCN	CTAOH + OH^-	14[c]	2.2

[a] Based on 10^3k_W 0.14 and 6.4 l mol s^{-1} for DNCB and DNCN respectively. [b] Ref. 5. [c] Ref. 4.

haviour, but no well defined break in plots of conductivity against concentration.[4]

Rate Constants in Aqueous Micellar Pseudophases.—The second-order rate constants k_M are in Table 3. They depend upon the values of parameters which are discussed in ref. 5. In this context we note that fractional binding of micellized bolaform(22)Br, per head group, is similar to that of single-headed micelles,[1c,20] which suggests that ion-binding is not very different in the various systems.

In fitting the data in bolaform(22)OH we had to use a much lower value of K'_{OH} than that which fits rate data in CTAOH.[4] This result suggests that the bolaform micelle may have an open structure, with considerable chain bending,[1] and therefore be less effective than a CTA micelle at binding OH^-. This observation is not in contradiction to the estimates of α for the halide ion micelles because we believe that micelles bind halide ions by both specific and non-specific, coulombic, interaction, whereas specific interactions play little part in the binding of OH^-. Analysis of micellar binding of counterions based on the Poisson–Boltzmann equation in spherical symmetry supports this supposition.[11e]

The binding constants K_s for DNCB appear to increase with increasing $[OH^-]$. There is precedent for this observation,[4] and we ascribe it to 'salting out' of DNCB from water by OH^-. Binding of DNCN should be similarly affected, but here fitting is relatively insensitive to K_s.

Despite approximations in the treatment the rate constants k_M (Table 3) are similar for bolaform(22) and CTAX micelles,[4,5] which supports the assumptions that the surfaces are similar in these various micelles.

Comparison can be made based on equation (4), where V_M is

$$k_2^m = k_M V_M \tag{4}$$

the molar volume element of reaction in the micelles, which we take as 0.14 dm^3 (estimates[6] of V_M range from 0.14 to 0.35 dm^3).

The micellar rate enhancements for reaction of OH^- with DNCB and DNCN are due largely to increased reactant concentrations at the micellar surfaces, with a modest effect due to increased reactivity, which is probably related to stabilization of a low charge-density ionic transition state by the cationic head groups of the micelle.[21]

Reactions in Solutions of Bolaform-(16) *and* -(12).—We did not treat the kinetic data in bolaform(16)OH, Br quantitatively (Tables 1 and 2). Yiv and Zana concluded that micelles of bolaform(16)Br have an open structure with penetration of water and folding of the chains.[1b] In that event the surface charge density should be low and because the micellar radius should also be low, so should the ability to bind counterions,[11c,22] which is consistent with the relatively low rate enhancements (Tables 1 and 2). However, Yiv and Zana estimated the fractional degree of ionization as *ca.* 0.5,[1b] which is not much larger than that for bolaform(22)Br, and is similar, per head group, to values for normal single-headed micelles with halide counterion, so we do not have sufficient information to explain all the kinetic results in the bolaform(16) system. However, as for normal micelles,[6] bromide ion inhibits the reaction by competing effectively with the reactive anion.

The different rate enchancements by the C-22 and C-16 and C-12 bolaform surfactants suggest that the former form aggregates similar to normal micelles whereas the latter form smaller aggregates which can, however, affect reaction rates. The chains in a bolaform micelle may be extended or bent,[1,2] and bending becomes easier with increasing chain length so that C-16, and especially C-12, bolaform should form only small aggregates.

Micellar reactions of polar materials occur at surfaces, and in comparing reactions in bolaform and CTAX micelles we are comparing the properties of the respective surfaces, but they are inevitably dependent upon the interactions of the surfactant chains in the micellar core as well as on interactions with counterions. The results with the C-16 and C-12 bolaforms show that submicellar assemblies can affect reactivity.

Acknowledgements

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

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Received 6th *February* 1986; *Paper* 6/262