Tetrahedron Vol 45, No 6, pp 1747 to 1754, 1989
Printed in Great Britain

0040-4020/89 $3 00+ 00

NUCLEOPHILICITY OF HALIDE IONS IN THE MICELLAR PSEUDOPHASE

HAMAD A.AL-LOHEDAN

Dept. of Chemistry, King Saud University, P.O.Box 2455,
Riyadh-11451, Saudi Arabia.

(*Received in UK* 15 *December* 1988)

Abstract - The reaction of Br^- or Cl^- with both n-butyl-4-nitrobenzenesulfonate and n-butyl-4-bromobenzenesulfonate 1a and 1b respectively is catalyzed by cationic micelles of cetyltrimethylammonium chloride or bromide (CTACl or CTABr respectively). The increase of rate constant with [surfactant] can be analyzed in terms of the concentration of substrate (1a - b) and halide ion in the micellar pseudophase, and the second-order rate constants in micellar and aqueous pseudophase are similar.

It is known that the rates of bimolecular reactions are strongly affected by micellar systems. This effect arises primarily from concentrating both reactants in the small volume of Stern Layer of micelles[1-5] and the variations of rate constants with [surfactant] can often be treated quantitatively in these terms[1-8]. A very useful and widely used approach to examin the distribution of hydrophilic ions between aqueous and micellar pseudophases is to assume that counterions compete for ionic sites on the micellar surface and that the fractions, β , of these sites which are neutralized by counterions is approximately constant[2,5]. This general approach has been applied successfully to rate and equilibrium constants of many reactions in aqueous micelles[9-11]. However, the treatment involves several parameters e.g. β , whose values are not known with certainty. In addition, interionic competion between, for example an inert ion Y^-, and a nucleophile X^-, may not be described accurately in terms of an ion-exchange model where subscripts W and M

$$X_M^- + Y_W^- \rightleftharpoons X_W^- + Y_M^- \quad \ldots\ldots\ldots \quad (1)$$

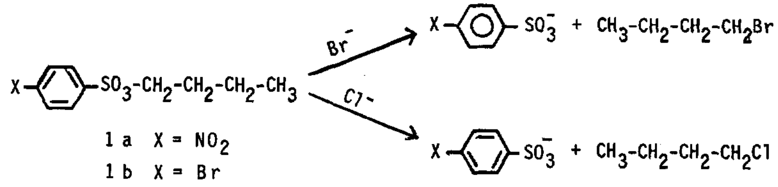
denote aqueous and micellar pseudophases respectively. The ion-exchange constant is given by

$$K_Y^X = [X_W^-][Y_M^-]/[X_M^-][Y_W^-] \quad \ldots\ldots\ldots \quad (2)$$

The problem of interionic competion can be eliminated by using a reactive ion surfactant, in which ionic reagent is the micellar counterion[12-14], so its concentration in the micellar pseudophase should be constant, provided that β, is constant, and the first-order rate constant k_ψ for the overall reaction should increase with increasing [surfactant] and become constant once substrate is fully micellar bound. This predicted behaviour is observed for reactions of H^+ in micellized alkanesulfonic acid[15], of N-alkylpyridinium ion in micellized CTACN[16] and for substitution by Br^- and Cl^- [17,18].

However, for reaction of very hydrophilic anions e.g. OH^-, F^-, or RCO_2^-, value of k_ψ increases with increasing [surfactant] even when the substrate is fully micellar bound[12,13]. The aim of the present work is to examine the micellar effects upon nucleophilic substitution by Cl^- or Br^- upon n-butyl-4-nitrobenzenesulfonate and n-butyl-4-bromobenzenesulfonate (1a-b) in solution of cetyltrimethylammonium chloride or bromide (CTACl or CTABr respectively (scheme 1)

Scheme 1



1 a X = NO_2
1 b X = Br

The reaction of (1a-b) with water is inhibited by cationic micelles which have unreactive counterions such as Mysylate so it makes minor contribution[20].

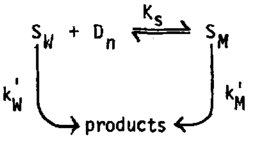
RESULTS AND DISCUSSION

Reaction in the Presence of Salt: The nucleophilicity of bromide is better than chloride ion in hydroxylic solvent, because hydrogen bonding reduces nucleophilicity of anions and the effects is greatest with small hydrophilic anions of high charge density[22,23]. We see this behaviour in our reactions (Table I and II) and the second-order rate constants for the reactions of Cl^- and Br^- with n-butyl-4-nitrobenzenesulfonate are $9.84 \times 10^{-5}\ m^{-1}\ s^{-1}$ and $2.25 \times 10^{-4}\ m^{-1}\ s^{-1}$ respectively. While the second-order rate constants for reactions of Cl^- and Br^- with n-butyl-4-bromobenzenesulfonate are $4.5 \times 10^{-5}\ M^{-1}\ s^{-1}$ and $7.2 \times 10^{-5}\ M^{-1}\ s^{-1}$ respectively(no corrections is made for the salt effects upon these reactions).

Reaction in Micellar Solutions: In the reactions of Cl^- or Br^- with substrate 1a and 1b the first-order rate constant k_ψ ,increase smoothly with increasing[CTACl] or [CTABr] (Figure 1 and 2). Also, k_ψ , increase with addition of common halide ion to the surfactant solutions (Figure 1 and 2). At high concentration of surfactant values of k_ψ tend to reach limits and as for reaction in water, Br^-,appears to be a better nucleophile than Cl^-. This differences are understandable because counterions are extensively hydrated in the water rich Stern Layer of a normal micelles[24].

Quantitative Treatment of Rate Effects: The variation of rate constant with [surfactant] is generally treated on the assumption that, S, is distributed between the aqueous and micellar pseudophases designated by subscripts W and M respectively (Scheme 2) and can react in each pseudophase, with first-order rate constants being K'_W and k'_M. The micellized surfactant (detergent) is designated D_n ,

Scheme 2



and its concentration is that of the total surfactant concentration, less that of monomeric surfactant (cmc), and K_s is the equilibrium constant for substrate binding (eq 3 and 4).

$$K_s = [S_M]/[S_W][D_n] \quad \text{.....} \quad (3)$$

$$[D_n] = [D_T] - \text{cmc} \quad \text{.....} \quad (4)$$

There is also a reaction with water, which makes a major contribution k_{H_2O} to the observed rate constant so we neglect it.

Provided that equilibrium is maintained between reactants in the pseudophases, the first-order rate constant is given by[25]

$$k_{\psi} = \frac{k'_W + k'_M K_s [D_n]}{1 + K_s [D_n]} \qquad \text{........ (5)}$$

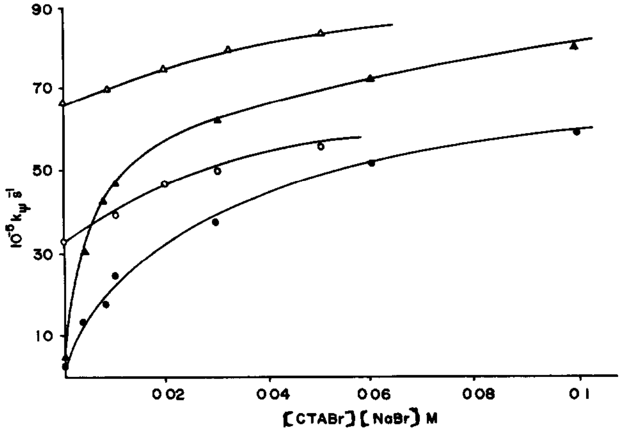


Figure 1 Reactions of n-butyl 4-Nitrobenzenesulfonate with Br̄, ▲ in CTABr, △ in 0.04 M CTABr + NaBr. ● For reactions of n-butyl 4-bromobenzenesulfonate with Br̄ in CTABr; o in 0 04 M CTABr + NaBr

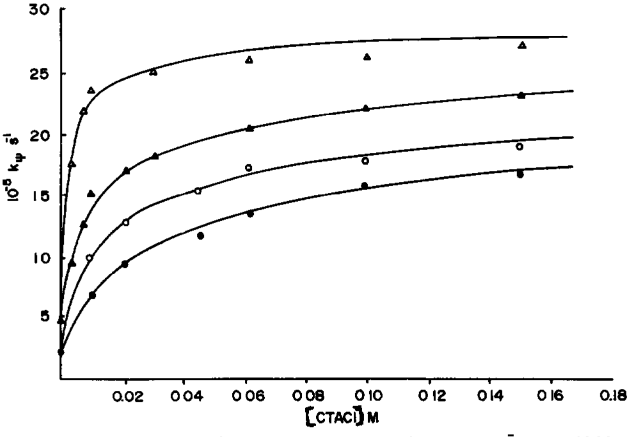


Figure 2 Reactions of n-butyl 4-Nitrobenzenesulfonate with Cl̄, ▲ in CTACl, △ in CTACl + 0.1 M NaCl ● for reactions of n-butyl 4-bromobenzenesulfonate with Cl̄ in CTACl, o in CTACl + 0.1M NaCl

These rate constants can be written in terms of the second-order rate constants k_W and k_M and the concentration of Cl^- and Br^- in each pseudophase eq. 6 and 7.

$$k'_W = k_W[X_W^-] \qquad \text{......... (6)}$$

$$k'_M = k_M m_X^s = k_M [X_M^-]/[D_n] = k_M \beta \qquad \text{......... (7)}$$

Table I. Reaction of n-butyl-4-nitrobenzenesulfonate in the absence of surfactant[a].

[Salt]M	NaCl	NaBr
0.02	4.9	5.2
0.08	5.5	6.6
0.15	6.2	7.9
0.2	6.7	9.5

[a] values of $10^5 k_\psi\ s^-$ at 25°C. In water $10^5 k_W = 4.6\ s^{-1}$.

Table II. Reaction of n-butyl-4-bromobenzenesulfonate in the absence of surfactant[a].

[Salt]M	NaCl	NaBr
0.02	1.95	2.10
0.08	2.20	2.5
0.15	2.52	2.95
0.2	2.72	3.5

[a] values of $10^4\ k_\psi\ s^{-1}$ at 25°C. In water $10^5\ k_W = 1.85\ s^{-1}$.

The rate constant, k_M , is defined by using concentration written as a mole ratio, m_X^s, which for a reactive ion surfactant is β.

The quantitative treatment of the rate data therefore involves estimation of the distribution of substrate between water and micelles, which depends on K_s and estimation of the concentration of Cl^- or Br^- in the micellar pseudophase.

The binding constants, K_s , cannot be measured directly because of reaction between substrates and halide ion, but comparison with the binding of similar, but unreactive solutes suggest that $K_s = 10^2\ M^{-1}$, for both CTACl and CTABr[2-9,18]. However, addition of salts to surfactant solution may increase K_s, by " salting out " nonionic solutes from the aqueous pseudophase and we considered this possibility in fitting the rate data[5,9,14,18].

The variation of k_ψ , with [surfactant] for reactions in some reactive ion surfactant, e.g. in CTACN[16] and some sulfonic acids[15] can be analyzed on the assumption that β is constant[15,16]. However, when the reactive ion is OH^- or F^-, k_ψ increases with increasing concentration of nucleophile or surfactant even when the substrate is fully micellar bound[12,14,15,26], but the distribution of counterion X^- between aqueous and micellar pseudophase can be fitted to eq. 8, i.e. to a mass action model[12-14,18].

$$K'_X = [X^-_M]/[X^-_W]([D_n]-[X_M]) \qquad \text{.................} (8)$$

Table III. Rate and equilibrium constant for reaction in CTABr[a].

Medium	Substrate	$K_s M^{-1}$	$10^4 k_M s^{-1}$	$10^5 k_2^m M^{-1}s^{-1}$	k_2^m/k_W
CTABr	1 a	115	10.2	14.4	0.66
0.04 CTABr + NaBr	1 a	130	10.3	14.5	0.66
CTABr	1 b	120	7.5	10.5	1.1
0.04 CTABr + NaBr	1 b	135	7.3	10.4	1.1

[a] Model i assumes a constant β of 0.8. The fit assumes a salt effect on substrate binding, see text.

Table IV. Rate and equilibrium constant for reaction in CTACl[a]

Medium	Substrate	$K'_X M^{-1}$	$K_s M^{-1}$	$10^4 k_M s^{-1}$	$10^5 k_2^m M^{-1} s^{-1}$	k_2^m / k_W
CTACl	1 a	230	115	2.9	4.1	0.91
CTACl + 0.1 M NaCl	1 a	230	130	3.0	4.2	0.93
CTACl	1 b	215	125	2.1	2.9	0.4
CTACl + 0.1 M NaCl	1 b	215	135	2.0	2.8	0.4

[a] We used model ii which is a mass action treatment with variable β

Equation 8 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. 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[9,11,27].

Therefore in treating our data we consider two possibilities (i) that β is constant over a wide range of surfactant or halide ion concentration as is often assumed[2], we apply this possibility on the reactions in CTABr. (ii) that β increases with increasing halide ion concentration, based on a model applied to micellar binding of relatively hydrophilic anions[12,14], we use this approximation for reactions in CTACl. The simplest assumption is that of a constant β, so that eq.5-7 gives :

$$k_\psi = \frac{k_W [X_W^-] + k_M K_s \beta [D_n]}{1 + K_s[D_n]} \qquad \text{..........} (9)$$

$$\frac{k_W ([X_T^-] - [X_M^-]) + k_M K_s \beta [D_n]}{1 + K_s[D_n]} \qquad \text{.........} (10)$$

$$\frac{k_W ([X_T^-] - [X_M^-]) + k_M K_s [X_M^-]}{1 + K_s [D_n]} \qquad \text{.........} (11)$$

where subscripts, T denotes the total concentration of X^-. With fully micellar bound substrate eq. 12 simplifies to

$$k_{\psi} = K_M \beta \qquad \ldots\ldots\ldots\ldots\ldots(12)$$

Reaction in CTABr: Equation 12 with a constant β (model i) fits the variation of k_{ψ} *with [CTABr] (figure 1) in terms of the parameters in Table III. We note that* the rate data can be fitted to other combination of these parameters provided that the variations are small[9,10].

However, the increase of k_{ψ} with added salt is inconsistent with a constant value of β eq. 8-11. One possibility is that added halide ion increase K_s , by "Salting out" the substrate from the aqueous pseudophase. There is precedence for such an effect[5,9], but it is small in other systems and too small to explain all our salt effects. Therefore, we did not explain our data for reactions of Cl^- in *terms of a constant* β[28].

For reaction in 0.04 M CTABr + NaBr the rate constants could be fitted to model I (figure 1), assuming constant β provided that we assumed that NaBr increased the binding constant of the substrates to the micelles, following eq. 13,i.e.with $b = 12M^{-1}$, assuming that NaBr "salts-out" the

$$K_s = 100\ (1 + b\,[NaBr] \qquad \ldots\ldots\ldots\ldots\ (13)$$

substrate from the aqueous pseudophase, cf.ref. 6,9 and 18. Although assumption of a constant β (midel i) is satisfactory for reactions in CTABr and CTABr + NaBr. we could not fit the rate data for reaction in CTACl and CTACl+NaCl in terms of this model without using high values of b, eq.13, e.g. greater than $40\,M^{-1}$ which is not reasonable.

We therefore conclude that β for CTACl increases with added Cl^-, although the effect is smaller than that apparently observed with CTAOH and CTAF[14,15,31], but it is close to that in CTAFor, CTAoAc[12].

Reactions in CTACl : To explain the variation of k_{ψ} with [CTACl] we assumed that β increases with increasing halide ion $[Cl^-]$ (model ii) eq.8. Equation 8 places formal limits on 0 and 1 on β , although the lower limit cannot be reached because there is always counterion present in aqueous pseudophase and the upper limit of 1 is reached only at counterion concentration beyond any reasonable limit[14]. In practice β would vary little with $[X^-]$ if $K'_X > 10^3\,M^{-1}$.

Equations 5 and 8 can be combined and a simple computer programme used to predict the variation of k_{ψ} with [CTACl] and added X^- and we were able to fit all the rate data for reaction in surfactant of CTACl and with added salt (figure 2) using the parameter given in Table IV.

Some variation of β with added counterion is not unreasonable because there is a distribution of micellar sizes in any given surfactant solution[29]. The larger micelles should be the more effective at attracting counterions and if added salt the size distribution toward larger micelles, it should also increase . Micellar growth depends upon the balance of surfactant-surfactant and surfactant-counterion interaction, and one would expect variation of micellar size to be largest when the counterions interact the least with the micellar head groups as with such hydrophylic ions as OH^- or F^-.

Comparison of Reaction in CTABr and CTACl: The rate surfactant profiles for reactions in CTABr can be fitted with assumption of constant β (Table III and figure 1) that is beacuse this approximation is satisfactory for an ion such as Br^- which binds strongly to cationic micelles, but it fails for Cl^- which binds less strongly than Br^- to micelles[9,11,27]. Therefore we use a mass action model to treat the rate surfactant profiles for reactions in CTACl (Table IV and figure 2). The values of K_X^- for Cl^- (Table IV) are reasonable in comparison with $K'_{OH} = 55\ M^{-1}$ and $K'_F = 40\ M^{-1}$ and $K'_{for} = 80\ M^{-1}$ for formate and acetate ion[12], because less hydrophilic ion such as Cl^- or Br^- should have larger binding constants.

The values of K_s are similar in both model. The second-order rate constants for reaction in the micellar and aqueous pseudophases, k_M and k_W, have different dimensions[5,31]. The second-order rate constant k_M is expressed in terms of concentration as a molar ratio of reactive anion to micellar head groups (eq. 7) where as for k_W the counterion is written conventionally, as moles of nucleophile per liter of aqueous pseudophase which is approximated as total solution. These rate constants can be compared by defining the volume element of reaction in the micelles, which we assume to be that of Stern Layer, with a molar volume of ca. 0.14 L[5,9,30]. Therefore, the second-order rate constant, k_2^m, $M^{-1}\ s^{-1}$ is given by

$$k_2^m = 0.14\ k_M \qquad \text{.............} \quad (14)$$

The values of k_2^m for reactions in the micellar Stern Layer are almost identical with those of k_W in water (Table III and IV). 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[2,18], so our overall conclusion would be little affected by choice of a different volume element of the reaction[18]. The similarity of k_2^m and k_W is understandable, because both substrate and halide ion should be located near the water reach micellar surface[2,24]. There are many example 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 two reactants in the micelle[18].

EXPERIMENTAL

Materials: The preparation of n-butyl-4-nitrobenzenesulfonate and n-butyl-4-bromobenzenesulfonate and purification of surfactant followed a standard methods[5,21].

Kinetics : All the reactions were followed spectrophotometrically in water at 25°C by the decrease of absorbance at 252 nm for n-butyl-4-nitrobenzenesulfonate and 265 nm for n-butyl-4-bromobenzenesulfonate. The rate constant did not change by adding $10^{-3}M$ HBr or HCl so there is no contribution from reaction with OH^-. For all reactions substrate was added as a solution in MeCN to the reaction mixture in a 1 cm cuvette so that the concentration of the substrate was $10^{-5}M$ and the solutions contain less than 0.1% MeCN. The first-order rate constant, k_ψ , are in a reciprocal seconds.

Acknowledgement: Support of this work by the Research Center, College of Science, King Saud University is greatly acknowledged.

REFERENCES

1. Cordes,E.H., Pure Appl. Chem., 1978,50,617.
2. Romsted,L.S. in "Micellizations, solubilization and Microemulsions", Mittal, K.L. ed.,Plenum,New York,1977,Vol.2,p.509.
3. Bunton,C.A.,Catal.Rev.Sci.,Eng.,1979,83,680.
4. Bunton,C.A. in "Solution Chemistry of Surfactant", Mittal,K.L. ed.,Plenum,New York,1979,Vol.2,p.519.
5. Al-Lohedan,H.A.,Ph.D. thesis, University of California,Santa Barbara,1981.
6. Al-Lohedan,H.A.,Arab Gulf Scient.Res.Math.Phys.Sci.,1977,A5(2),p.191.
7. Martinek,K.,Yatsimirski,A.K.,Levashov,A.V.,Berezin,I.V., In ref.2, p.489.
8. Cuccovia,I.M.,Schroter,E.H.,Monterio,P.M.,Chaimovich,H.,J.Org.Chem.,1978,43, 2248.
9. Al-Lohedan,H.A., Bunton,C.A., Romsted,L.S., J.Phys.Chem.,1981,85,2123.
10. Al-Lohedan,H.A., Bunton,C.A., Romsted,L.S., J.Org.Chem.,1982,47,3528.
11. Quina,F.H., Chaimovich,H., J.Phys.Chem., 1979,83,1844.
12. Al-Lohedan,H.A., Bunton,C.A., Romsted,L.S., J.Org.Chem., 1982,7,1160.
13. Al-Lohedan,H.A., Tetrahedron,1987,Vol.43,No.2,345.
14. Bunton,C.A., Gan,L.H., Meffot,J.R., Romsted,L.S., Savalli,G., J.Phys.Chem., 1981, 85,4118.
15. Bunton,C.A., Romsted,L.S., Savelli,G., J.Am.Chem.Soc.,1979,101,1253.
16. Bunton,C.A., Romsted,L.S., Thamavit,C., J.Am.Chem.Soc.,1980,109,3900.
17. Bunton,C.A., Romsted,L.S., in "Solution Behaviour of Surfactants, Theoretical and Applied Aspects", Fendler,E.J., Mittal,K.L., ed. Plenum Press, New York, 1982, Vol.2,p.975.
18. Al-Lohedan,H.A., Bunton,C.A., Moffatt,J.R., J.Phys.Chem.,1983,87,332.
19. Al-Lohedan,H.A., Bunton,C.A., Mhala,M., J.Am.Chem.Soc., 1982,104,6654.
20. Al-Lohedan,H.A., unpublished result .
21. Vogel,I., in "A Textbook of Practical Organic Chemistry", 3rd edition,Longman, Toronto, 1956,p.820.
22. Winstein,S., Savedoff,L.G., Smith,S., Stevens,I.D.R., Gall,J.S., Tetrahedron Letter., 1960,24.
23. Parker,A.J., J.Chem.Soc. A, 1966,220 Chem.Rev.,1969,68,1.
24. Stigter,D., J.Phys.Chem.,1964,68,3603.
25. Menger,F.M., Portnoy,C.E., J.Am.Chem.Soc.,1967,89,4968.
26. Bunton,C.A., Frankson,J., Romsted,L.S., J.Phys.Chem.,1980,84,2607.
27. Bartet,E., Gamboa,C., Sepulveda,L., J.Phys.Chem.,1980,84,272, Gamboa,C., Sepulveda,L., Soto,R., Ibid, 1981,85,1429.
28. Preparation at high concentration of NaBr and CTABr limits our work.
29. Tanford,C.H., in "THe Hydrophobic Effect", Wiley Interscience, New York,1980, 2nd Ed., Chapter 6-8.
30. Bunton,C.A., Carrasco,N., Huang,S.K., Paik,C.H., Romsted,L.S., J.Am.Chem.Soc., 1978,100,5420.
31. Al-Lohedan,H.A., J.Phys.Chem., 1987,91,4524.