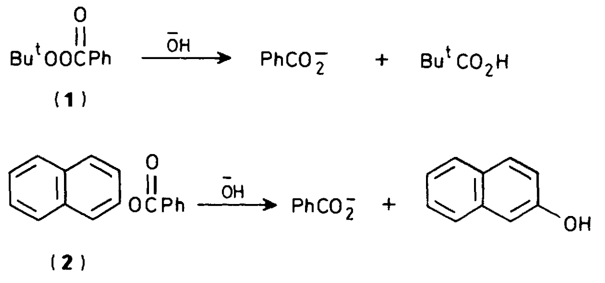
Quantitative Treatment and Micellar Effects in the Reaction of t-Butyl Perbenzoate and 2-Naphthyl Benzoate

Hamad A. Al-Lohedan*
Dept. of Chemistry, King Saud University, P.O. Box 2455, Riyadh-11451, Saudi Arabia

The basic hydrolysis of t-butyl perbenzoate and 2-naphthyl benzoate has been studied in cationic micelles of cetyltrimethylammonium chloride or hydroxide (CTACl or CTAOH, respectively). The increase in rate constant with surfactant concentration can be analysed in terms of the concentration of (**1**), (**2**), and hydroxide ion in the micellar pseudophase; the determined second order rate constants in the micellar pseudophase are smaller than the second order constants in water.

Micellar effects upon bimolecular reactions in aqueous systems have been extensively studied,[1] and the variation in rate constant with surfactant concentration has been explained quantitatively by considering the distribution of both reagents between aqueous and micellar pseudophases and the second order rate constant in each pseudophase.[2-8] 2-Naphthyl benzoate and t-butyl perbenzoate are convenient substrates for a study of micellar effects on the reaction rate because the reaction mechanisms are well understood[9-11] and the reaction can be easily followed in dilute solution. We examined micellar effects in the reactions of t-butyl perbenzoate and 2-naphthyl benzoate with OH^- in water (Scheme 1). These substrates are very hydrophobic so they should bind readily to micelles.



Scheme 1.

Reactions were carried out in aqueous solutions of cetyltrimethylammonium chloride or hydroxide (CTACl or CTAOH, respectively). Typically the rate constants for bimolecular reactions passed through maxima with increasing surfactant concentration (with constant nucleophile concentration in the presence of an inert surfactant counter-ion).[2-8]

In the carboxylic ester deacylation by OH^- in CTACl the rate maxima can be ascribed to a combination of competition between OH^- and Cl^- for micelle and distribution of the substrate between water and micelles. However, if only the reactive counter-ion were present in the solution the rate constant should become constant once all the substrate is micellar bound, provided that the micelle is saturated with counter-ion. This behaviour has been observed for reactions involving protons,[12] for nucleophilic addition by CN,[13] and for substitution by Br.[14,15] Nucleophilic reactions in CTAOH and CTAF do not fit this pattern[12,14-18] and it appears that here the concentration of micellar bound OH^- or F^- increases with increasing total concentration. We were interested, therefore, in studying the reactions of other substrates in micellised reactive ion surfactants, with OH^- as nucleophile, in CTACl with added inert counter-ion.

Table 1. Salt effect on reaction of substrates (**1**) and (**2**) in water.[a]

$[NaCl]/mol\ dm^{-3}$	k_ψ (1)	k_ψ (2)
0.005	0.34	0.61
0.01	0.31	0.58
0.02	0.29	0.55
0.05	0.26	0.52
0.1	0.24	0.49
0.15	0.23	0.47
0.2	0.22	0.46

[a] Value of k_W ($mol^{-1}\ dm^3\ s^{-1}$) at 25 °C with 5×10^{-5} $mol\ dm^{-3}$ of substrate.

Experimental

Materials.—The preparation or purification of CTACl and CTAOH followed standard methods.[17,18,19] t-Butyl perbenzoate and 2-naphthyl benzoate were of reagent grade and were used with purification.

Kinetics.—The reactions were followed spectrophotometrically using a Perkin-Elmer spectrophotometer. All reactions were followed in water at 25.0 °C. Both substrates were added as a solution in MeCN to the reaction mixture in a 1 cm cuvette so that the concentration of t-butyl perbenzoate or 2-naphthyl benzoate was 5×10^{-5} $mol\ dm^{-3}$ and the solution contained 0.1% MeCN. Reaction of t-butyl perbenzoate was followed at 229 nm and that of 2-naphthyl benzoate at 218 nm.

The pseudo-first order rate constants k_ψ are in s^{-1}. The spontaneous water catalysed reactions make only a minor contribution,[16] and we neglect them in the analysis.

Results

Reactions in Water.—The values for the second order rate constants (k_W) for the reactions of t-butyl perbenzoate and 2-naphthyl benzoate with OH^- at 25.0 °C were 0.36 $mol^{-1}\ dm^3\ s^{-1}$ and 0.65 $mol^{-1}\ dm^3\ s^{-1}$, respectively. Reaction of NaOH with t-butyl perbenzoate gave sodium benzoate and t-butyl hydroperoxide, which is very stable.[9] Added electrolyte slowed down the reaction, as is general for reactions between ions of opposite charge (Table 1).

Reaction in CTACl.— Figures 1 and 2 present rate constant data for micellised CTACl catalysed reactions with OH^-. In general, k_ψ passed through maxima with increasing [CTACl] and constant [OH^-]; added Cl^- inhibited the reaction by competing with the reactive anion for the micelle[6,8,16]

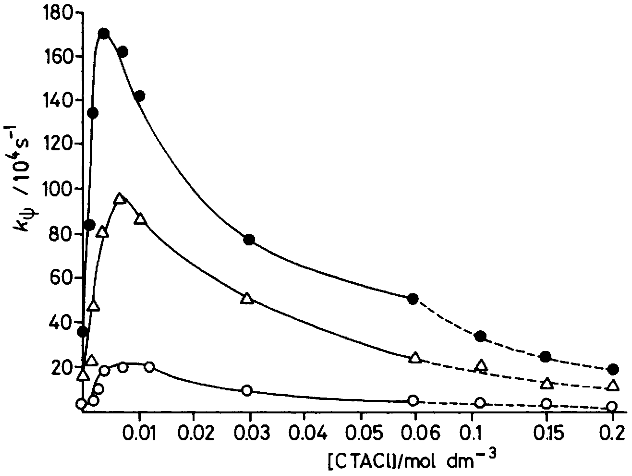


Figure 1. Variation of the first-order rate constant k_ψ with [CATCl] for the reaction of t-butyl perbenzoate with NaOH: (○) 10^{-3} mol dm^{-3} NaOH; (△) 5 × 10^{-3} mol dm^{-3} NaOH; (●) 10^{-2} mol dm^{-3} NaOH.

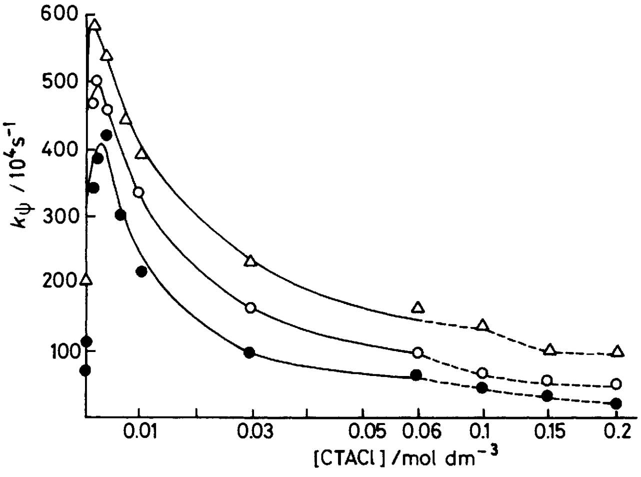


Figure 2. Variation of the first-order rate constant k_ψ with [CATCl] for the reaction of 2-naphthyl benzoate with NaOH: (●) 10^{-2} mol dm^{-3} NaOH; (○) 2 × 10^{-2} mol dm^{-3} NaOH; (△) 3 × 10^{-3} mol dm^{-3} NaOH.

Table 2. Salt effect upon reactions of substrates (**1**) and (**2**) in CTACl.[a]

	10^4k_ψ	
[NaCl]/mol dm^{-3}	(**1**)	(**2**)
0.002	92	138
0.007	81	127
0.01	73	116
0.03	67	108
0.05	61	100
0.07	57	95
0.1	54	88

[a] Value of k_ψ/s^{-1} at 25 °C, in NaOH (0.01 mol dm^{-3}) and CTACl (0.02 mol dm^{-3}).

(Table 2). The rate surfactant profiles are similar for both substrates.

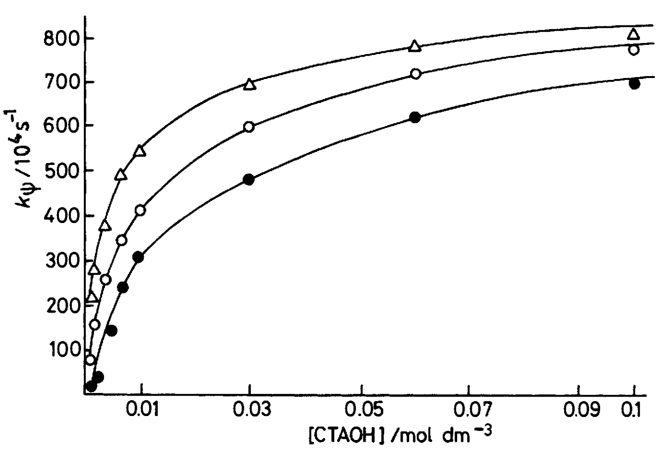


Figure 3. Variation of k_ψ for reaction of t-butyl perbenzoate in CTAOH: (●) in absence of NaOH; (○) 0.01 mol dm^{-3} NaOH; (△) 0.03 mol dm^{-3} NaOH.

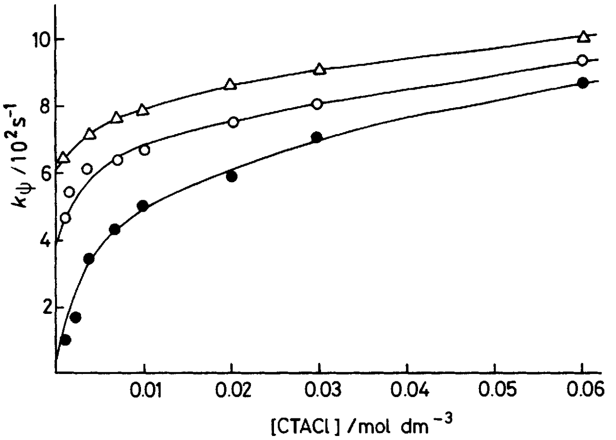


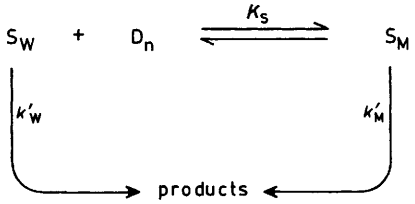
Figure 4. Variation of k_ψ for reaction of 2-naphthyl benzoate with [CTAOH]: (●) in absence of NaOH; (○) 0.02 mol dm^{-3} NaOH; (△) 0.04 mol dm^{-3} NaOH.

Reactions in CTAOH.—(*a*) *t-Butyl perbenzoate.* The pseudo-first order rate constants increase smoothly with increasing [CTAOH]. The addition of OH$^-$ to the surfactant solution increases k_ψ, but only to a small extent, and at higher surfactant concentration. At high surfactant or nucleophile concentration, k_ψ tends toward limiting values (Figure 3) (*cf.* refs. 14, 16, 18, and 19). However, t-butyl perbenzoate is hydrophobic and should be fully micellar bound at surfactant concentrations well below those corresponding to limiting values of k_ψ.[16,20]

(*b*) *Naphthyl benzoate.* The variation of k_ψ with [CTAOH] is very similar to that found for the reaction of t-butyl perbenzoate and added OH$^-$ increases the reaction rate (Figure 4).

Discussion

It is generally assumed that reaction can take place in the aqueous micellar pseudophase[21] (Scheme 2). The micellised surfactant is denoted as D_n and its concentration is assumed to be given by [D] − cmc, where D is the surfactant and cmc the



Scheme 2.

critical micelle concentration which is assumed to be the concentration of monomeric surfactant.

Reactions in CTAOH.—We assume that the distribution of substrate between aqueous and micellar pseudophase follows Scheme 2, so that the overall rate constant is given[21] by equation (1), where k'_W and k'_M are the pseudo-first order rate constants in the aqueous and micellar pseudophase, respectively and K_s is the binding constant of the substrate written in terms of the concentration of micellised surfactant $[D_n]$. Concentrations are expressed in terms of the total solution volume.

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

In equation (1), k'_W and k'_M can be written in terms of the second-order rate constants, k_W and k_M, and the concentration of OH^- in each pseudophase, equations (2) and (3).

$$k'_W = k_W[OH] \qquad (2)$$

$$k'_M = k_M m^s_{OH} = k_M[OH_M]/[D_n] = k_M\beta \qquad (3)$$

The rate constant k_M is defined by using concentration written as a mole ratio m^s_{OH}. Equations (1)–(3) can be used to derive equations (4) and (5).

$$k_\psi = \frac{k_W[OH^-_W] + k_M K_s m^s_{OH}[D_n]}{1 + K_s[D_n]} \qquad (4)$$

$$k_\psi = \frac{k_W[OH_W] + k_M K_s[OH_M]}{1 + K_s[D_n]} \qquad (5)$$

For a reactive ion surfactant such as CTAOH the molar ratio m^s_{OH} of bound ion to micellar head groups is given by β, the fractional extent of charge neutralisation of the head groups.[12,13,16,18] Therefore, if β is independent of the concentration of the surfactant or added reactive ion, OH^-, [6,22] equation (6) holds once the substrate is fully micellar bound,

$$k_\psi = k_M\beta \qquad (6)$$

and k_ψ should then reach a constant value. This behaviour is found for reactions in some reactive ion surfactants, *e.g.* in CTACN,[13,23] CTABr,[14,16] CTAF,[16,23] and some sulphonic acids.[12] 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.[16,18,24] We see this aspparently anomalous behaviour for the reaction of t-butyl perbenzoate and 2-naphthyl benzoate with OH^- in Figures 3 and 4. Therefore, for a number of reactions the rate-surfactant profiles cannot be explained in terms of the simple model which assumes that β remains constant. They can, however, be fitted to a model which assumes that the apparent value of β increases with increasing concentration of the reactive counter-ion.[18,19]

The distribution of the reactive counter-ion OH^- between the aqueous and micellar pseudophases is written in terms of equation (7), where K'_{OH} can be regarded as a binding constant

$$K'_{OH} = [OH_M]/[X^-_W]([D_n] - [OH_M]) \qquad (7)$$

assumed to be independent of the charge neutralization of the micelle.

Equations (6) and (7) can be combined and a simple computer program used to predict the variation of $[OH_M]$ with surfactant concentration and added OH^-, and the variation of k_ψ can therefore be predicted. The second order rate constants, k_W, are measured directly and k_M, K_s, and K'_{OH} are treated as adjustable parameters. However, for dephosphorylation and aromatic nucleophilic substitution in CTAOH, $K'_{OH} = 55$ mol^{-1} dm^3 (ref. 18), and we use this value here. The critical micelle concentration, cmc, is also treated as an adjustable parameter, although its value in the kinetic systems is assumed to be similar to that of CTAOH or similar C_{16} surfactants in water. Most of our experiments were performed at relatively high surfactant concentrations where the simulated rate surfactant profiles are insensitive to the cmc and where substrates are strongly micellar bound and uncertainties in K_s are relatively unimportant, but we nevertheless take $K_s = 850$ and 2 300 mol^{-1} dm^3 for t-butyl perbenzoate and 2-naphthyl benzoate, respectively (Table 3). The cmc was taken to be 10^{-3} mol dm^{-3} for CTAOH. Changes in these values had no effect except in very dilute surfactant.

The variation of k_ψ for reactions of the substrate in solutions of CTAOH can be simulated by using this treatment and the fit is illustrated in Figures 3 and 4 where the solid lines are calculated. The treatment can also be applied to experiments with added OH^-. The parameters that best fit the kinetic results for reactions of substrates (**1**) and (**2**) in CTAOH are presented in Table 3.

Reactions in CTACl.—The variations of k_ψ with surfactant concentration (Figures 1 and 2) can be treated quantitatively by means of the pseudophase ion-exchange model based on equation (8); the concentration of the micellar bound nucleophilic anion OH^- was calculated using the ion-exchange equilibrium (8).[6,8]

$$OH^-_M + X^-_W \rightleftharpoons OH_W + X^-_M$$

$$K^{OH}_X = [OH^-_W][X^-_M]/[OH^-_M][X^-_W] \qquad (8)$$

The values of ion-exchange constants have been estimated by several methods. One approach is to use physical methods. In favourable cases electrochemistry can be useful[25,26] or an indicator such as arenesulphonate ion can be used because of its spectral change on binding to a micelle.[27] Other methods include ultrafiltration or the use of thiocyanate ion as indicator.[28]

The other general approach is to simulate the variation of rate or equilibrium constant with surfactant concentration by taking the ion-exchange constant as an adjustable parameter.[18,29,30] These various methods agree quantitatively that Br^- or Cl^- binds much more strongly than OH to cationic micelles, but nevertheless values of K^{OH}_{Cl} range from *ca.* 3.5–5.[31] There is a more fundamental problem which is that the treatments contain a variety of adjustable parameters, and the data can often be fitted by various combinations of these parameters.[8,29]

The general approach in fitting the variation of k_ψ with surfactant or salt concentration is to use equation (8) and the mass balance relation with assumed values of K^{OH}_{Cl}, to calculate $[OH^-_M]$ and $[OH^-_W]$, to insert these values into the rate equation, using assumed values of k_M and K_s and the measured k_W, and to simulate the variation of k_ψ with, *e.g.*, [CTACl]. The parameters that best fit our kinetic data for substrates (**1**) and (**2**) are illustrated in Table 4.

A major problem with this analysis of the rate or equilibrium data in CTACl or similar surfactants is that its application depends on the assumption that β is constant, despite changes in concentrations of surfactant or of added electrolyte.[6,29] For example, if the apparent value of β for

Table 3. Parameters that best fit the kinetic results for substrates (**1**) and (**2**) in CTAOH.[a]

Substrate	Medium	k_M/s^{-1}	K_s/mol^{-1} dm^3	K'_{OH}
(**1**)	CTAOH	0.11	800	55
(**1**)	CTAOH + 0.01 mol dm^{-3} NaOH	0.11	850	55
(**1**)	CTAOH + 0.03 mol dm^{-3} NaOH	0.11	850	55
(**2**)	CTAOH	0.11	2 200	55
(**2**)	CTAOH + 0.02 mol dm^{-3} NaOH	0.12	2 300	55
(**2**)	CTAOH + 0.04 mol dm^{-3} NaOH	0.12	2 300	55

[a] At 25.0 °C and cmc = 7×10^{-4} mol dm^{-3}.

Table 4. Parameters that best fit the kinetic results for substrates (**1**) and (**2**) in CTACl.[a]

Substrate	[OH]/mol dm^{-3}	k_M/s^{-1}	K_s/mol^{-1} dm^{-3}	K^{OH}_{Cl}	β
(**1**)	1×10^{-3}	0.10	750	4	0.8
(**1**)	5×10^{-3}	0.10	800	4	0.8
(**1**)	1×10^{-2}	0.09	800	4	0.8
(**2**)	1×10^{-2}	0.12	2 100	5	0.8
(**2**)	2×10^{-2}	0.11	2 100	5	0.8
(**2**)	3×10^{-2}	0.10	2 100	5	0.8

[a] At 25.0 °C and cmc = 3×10^{-3} mol dm^{-3}.

Table 5. Second-order rate constants in water and in micelles.

Substrate	k_M/s^{-1}	k_2^m/mol^{-1} dm^3 s^{-1}	k_2^m/k_W
t-Butyl perbenzoate	0.11	0.0154	0.042
2-Naphthyl benzoate	0.12	0.017	0.026

CTAOH and similar surfactants varies with concentration of surfactant or counter-ion in the way that we suggest, the ionic exchange equation (8) and associated mass balance relation may be no more than a first approximation. We note that the concentration of counter-ion in the aqueous pseudophase [equation (8)] depends critically upon the fractional degree of ionization of the micelle $\alpha = 1 - \beta$.[6] The assumed constancy of β is probably an approximation, even when Cl$^-$, for example, is the only counter-ion in solution.[22,32]

Comparison of Reactions in CTACl *and* CTAOH.—The treatment of reactions in CTACl with added nucleophile, equation (8), and those in CTAOH, equations (5)–(7), appears to be based on completely different premises and use of different approximations, but nonetheless, they lead to similar values of such parameters as k_M and K_s. Application of the ion-exchange equation to the rate surfactant profiles is typically dependent on the assumption that β is constant. This assumption appears to fail when the only counter-ion in solution is hydrophilic with a high charge density, *e.g.*[12,18,19] OH$^-$ or F$^-$, but it is probably reasonably satisfactory when the counter-ion is less hydrophilic, *e.g.*[13–16] Br$^-$, RCO$_2^-$, or CN$^-$. Equation (7) predicts that β will vary little with counter-ion concentration when K'_{OH} is large.[17–19] Therefore, the addition of a weakly bound anion, *e.g.* OH$^-$ to a solution of CTACl, for example, may not have a large effect on ionic binding to micelle, as given by β, so that the ion-exchange model is applicable.

The variable extent of the binding of reactive hydrophilic counter-ions to a micelle is expressed in equation (7), leading to a reasonable fit between observed and predicted rate-surfactant profiles (Figures 3 and 4, Table 3) suggesting that equation (7) describes the distribution of counter-ions between aqueous and micellar pseudophases. However, this distribution may be governed by a wide distribution of micellar sizes, ranging from relatively small micelles, which bind the counter-ion weakly, to normal-sized micelles, which bind it more strongly.[14,33] The size distribution could be much greater when the counter-ion is hydrophilic and weakly bound, *e.g.* with OH$^-$, than when it is more hydrophobic and relatively strongly bound, as with Cl$^-$ or Br$^-$, but an increase in counter-ion concentration should, in any event, increase micellar size[16] and counter-ion binding. Each treatment, therefore, appears to have its own limited range of applicability and cannot be applied outside that range.

Rate Constants in Aqueous and Micellar Pseudophases.—The second-order rate constant, k_M, of reactions in the micellar pseudophase have the dimensions of reciprocal time, because the concentration of OH$^-$ is written as a mole ratio. This choice of units allows an unambiguous definition of concentration in the micellar pseudophase, but k_M cannot then be compared directly with second-order rate constants in water k_W, the units of which are generally mol^{-1} dm^3 s^{-1}. A comparison can be made provided we specify the volume element for the reaction in the micellar pseudophase, which could be that of the micellar or of its Stern layer. Elsewhere the molar volume of the Stern layer of CTABr and similar micelles has been assumed[3,29] to be 0.14 dm^3 mol^{-1} so that

$$k_2^m = 0.14 k_M \qquad (9)$$

and k_2^m/mol^{-1} dm^3 s^{-1} can now be compared directly with k_W.

The second-order rate constants for reactions of t-butyl perbenzoate or 2-naphthyl benzoate with OH$^-$ are considerably smaller in micelles than in water (Table 5). These results are quite close to those for the reaction of benzoic anhydride with OH$^-$ in CTABr[16] while for reaction of bis(4-nitrophenyl) carbonate k_M and k_W are similar;[16] this could be due to their being located in different regions of the micelle. For example the polar nitro-groups of the carbonate might cause it to reside on the average in a more aqueous region of the micelle than that occupied by t-butyl perbenzoate, 2-naphthyl benzoate, or benzoic anhydride and the OH$^-$ should be largely near the water-rich micellar surface. This explanation is supported by the observation that micelles of CTACl or CTABr inhibit sharply the spontaneous hydrolysis of t-butyl perbenzoate, 2-naphthyl benzoate,[34] and benzoic anhydride[16] but they weakly inhibit hydrolysis of bis(4-nitrophenyl) carbonate. The micellar structure is not uniform, and recent treatments suggest that the hydrocarbon core is ordered at the centre and liquid-like on the exterior and that part of the core is exposed to water.[35] In addition the somewhat different geometries of the reacton centres of the substrates may influence the rate constants for nucleophilic attack in the micelles as compared with those in water.

Acknowledgements

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References

1 For general references on micellar rate effects, see refs. 2–4.

2 J. H. Fendler and E. J. Fendler, 'Catalysis in Micellar and Macromolecular Systems,' Academic Press, New York, 1975.

3 C. A. Bunton, *Catal. Rev. Sci., Eng.*, 1979, 20, 1.

4 E. H. Cordes, *Pure Appl. Chem.*, 1978, **50**, 617.

5 K. K. Martine, A. K. Yatsimirksi, A. V. Levashove, and I. V. Berezin, in 'Micellization, Solubilization and Microemulsion,' ed. K. L. Mittal, Plenum Press, New York, 1977, vol. 2, p. 489.

6 L. S. Romsted, ref. 5, p. 509.

7 M. Almgren and R. Rydholm, *J. Phys. Chem.*, 1979, **83**, 360.

8 H. A. Al-Lohedan, Ph.D. Thesis, University of California, Santa Barbara, 1981.

9 E. Koubek, M. L. Haggett, C. J. Battaglia, K. M. Ibne-Rasa, H. Y. Pyun, and J. O. Edwards, *J. Am. Chem. Soc.*, 1963, **85**, 2263.

10 A. L. Underwood and E. W. Anacker, *J. Phys. Chem.*, 1984, **88**, 2390.

11 W. P. Jencks, 'Catalysis in Chemistry and Enzymology,' McGraw-Hill, New York, 1969, Ch. 10.

12 C. A. Bunton, L. S. Romsted, and G. Savall, *J. Am. Chem. Soc.*, 1979, **101**, 1253.

13 C. A. Bunton, L. S. Romsted, and C. Thamavit, *J. Am. Chem. Soc.*, 1980, **102**, 3900.

14 C. A. Bunton and L. S. Romsted, in 'Solution Behaviour of Surfactant, Theoretical and Applied Aspects,' eds. E. J. Fendler and K. L. Mittal, Plenum Press, New York, 1982, vol. 2, p. 975.

15 H. A. Al-Lohedan, C. A. Bunton, and J. R. Moffatt, *J. Phys. Chem.*, 1983, **87**, 332.

16 H. A. Al-Lohedan and C. A. Bunton, *J. Org. Chem.*, 1982, **7**, 1160.

17 H. A. Al-Lohedan, *Tetrahedron*, 1987, vol. 43, no. 2, p. 345.

18 C. A. Bunton, L. H. Gan, J. R. Moffatt, L. S. Romsted, and G. Savalli, *J. Phys. Chem.*, 1981, **85**, 4118.

19 H. A. Al-Lohedan, *J. Phys. Chem.*, 1987, **91**, 4524.

20 F. M. Menger, H. Yoshinagu, K. S. Venkatasubban, and A. R. Das, *J. Org. Chem.*, 1981, **46**, 415.

21 F. M. Meneger and C. E. Protnoy, *J. Am. Chem. Soc.*, 1967, **89**, 4968.

22 G. Gunnarsson, B. Jonsson, and H. Wennerstrom, *J. Phys. Chem.*, 1980, **84**, 3114.

23 F. Ortega and E. Rodenas, *J. Phys. Chem.*, 1986, **90**, 2408.

24 S. Vera and E. Rodenas, *Tetrahedron*, 1986, **2**, p. 143.

25 J. W. Larsen and L. Magid, *J. Am. Chem. Soc.*, 1974, **96**, 5774.

26 C. A. Bunton, K. Ohmenzetter, and L. Sepulveda, *J. Phys. Chem.*, 1977, **81**, 2000.

27 D. Bartet, C. Gamboa, and L. Sepulveda, *J. Phys. Chem.*, 1980, **84**, 272.

28 C. Gamboa, L. Sepulveda, and R. Soto, *J. Phys. Chem.*, 1981, **85**, 1429.

29 H. A. Al-Lohedan, C. A. Bunton, and L. S. Romsted, *J. Phys. Chem.*, 1981, **85**, 2123.

30 H. A. Al-Lohedan, *Arab Gulf J. Scient. Res. Math. Phys. Sci.*, 1987, **A5(2)**, 191.

31 H. A. Al-Lohedan, C. A. Bunton, and L. S. Romsted, *J. Org. Chem.*, 1982, **47**, 3528.

32 A. Rohde and E. Sackmann, *J. Phys. Chem.*, 1980, **84**, 1598.

33 C. A. Bunton, J. Frankson, and L. S. Romsted, *J. Phys. Chem.*, 1980, **84**, 2607.

34 H. A. Al-Lohedan, unpublished results.

35 K. A. Dill and P. Flory, *Proc. Natl. Acad. Sci. U.S.A.*, 1981, **78**, 676.

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