

This article was downloaded by:

On: 29 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

MICELLAR EFFECTS UPON ACID CATALYZED HYDROLYSIS OF TRIPHENYLPHOSPHITE

Hamad A. Al-lohedan^a

^a Department of Chemistry, King Saud University, Riyadh, Saudi Arabia

To cite this Article Al-lohedan, Hamad A.(1991) 'MICELLAR EFFECTS UPON ACID CATALYZED HYDROLYSIS OF TRIPHENYLPHOSPHITE', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 63: 3, 261 — 271

To link to this Article: DOI: 10.1080/10426509108036829

URL: <http://dx.doi.org/10.1080/10426509108036829>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

MICELLAR EFFECTS UPON ACID CATALYZED HYDROLYSIS OF TRIPHENYLPHOSPHITE

HAMAD A. AL-LOHEDAN

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

(Received April 26, 1991; in final form July 25, 1991)

Acid hydrolysis of triphenylphosphite (1) are effectively catalyzed by anionic micelles of sodium lauryl sulfate (NaLS), alkylhydrogensulfate (2), tetradecanesulfonic acid (3a) and p. decyloxybenzenesulfonic acid (3b). Cationic micelles of cetyltrimethylammonium chloride (CTACl) inhibit the reaction. Rate effects were analyzed quantitatively in terms of distribution of reactants between water and the micelles; and the effect of added HCl or salt can be explained quantitatively in these terms.

Key words: Hydrolysis of triphenylphosphite; acid catalysis; micellar effects.

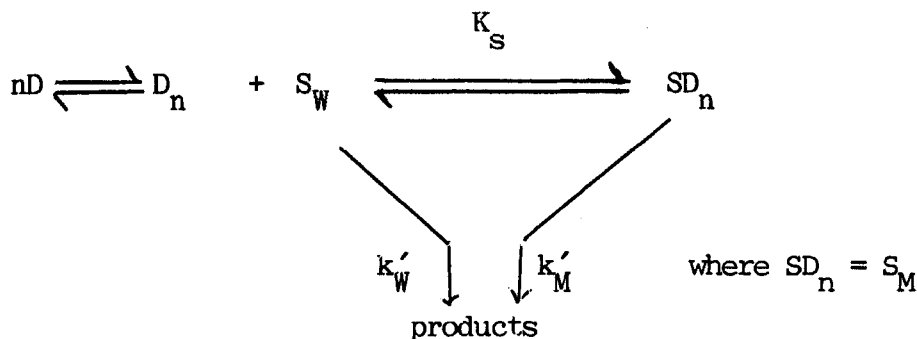
INTRODUCTION

Micellar catalysis of bimolecular reactions is generally rationalized in terms of reactions occurring either in the micellar or aqueous pseudophase.^{1–8} The first qualitative application of this model was to the inhibition of ester saponification by anionic micelles⁹ and catalysis of spontaneous hydrolysis of dinitrophenyl phosphate¹⁰ and sulfate¹¹ by cationic micelles. Many of the reactions which are catalyzed by micelles are pH dependent.^{12–14} For some reactions the rate changes with pH until all the substrate is converted into the reactive species and is then independent of pH, as in unimolecular hydrolysis of phosphate esters¹⁰ or decarboxylation,¹⁵ but often the hydrogen or hydroxide ions act as general catalysts.

Some of the kinetic work on micellar catalyzed reactions involving hydrogen or hydroxide ions has been done in buffer solutions, and often with added salt.¹⁶ Ionic micelles perturb buffer equilibria,¹⁸ and added salts may introduce further complications. For example, by lowering the cmc, reducing the surface potential, increasing micelle size and generally reducing reaction rate.^{3,16–18}

The pseudophase model assumes that changes in micellar shape or size are not important, so that only those factors which control the distribution of reactants will significantly affect the observed reaction rate. We selected reactions which would not require use of buffer because buffer effects are particularly difficult to interpret. However, even with all these problems, both the rate maxima in the rate-surfactant profiles and inhibition by added nonreactive counterions can be qualitatively interpreted by considering competition between reactive and non-reactive counterions for “sites” on the micelle surface.³

For micellar catalyzed bimolecular reactions it is necessary to consider the distribution of both reactants between the aqueous and micellar pseudophases. (Scheme I).



SCHEME I

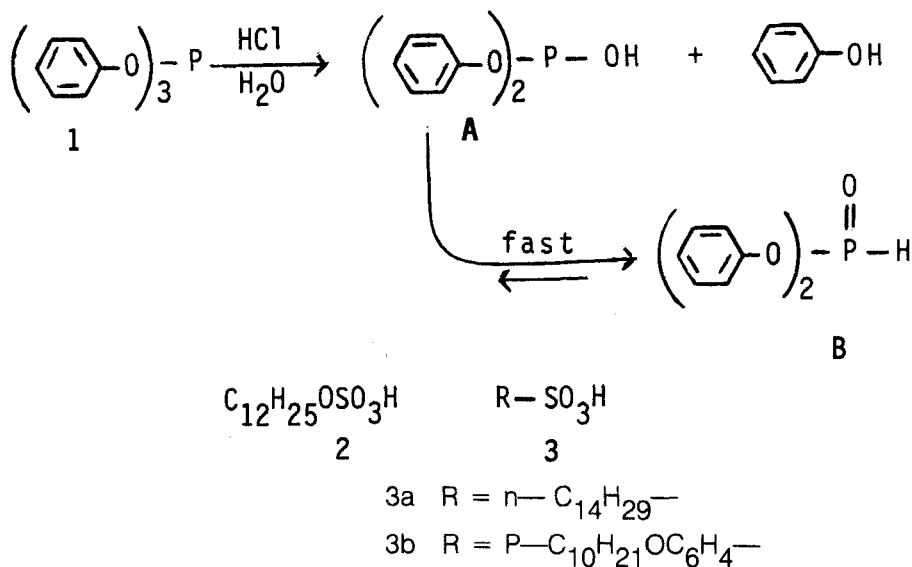
In Scheme I, S denotes organic substrate, D_n , micellized surfactant, and K_s the binding of S to D_n . The subscripts W and M denote water and micellar pseudophases, respectively, m_H^s is the mole ratio of bound H^+ to micellized surfactant, and k'_W and k'_M are the first-order rate constants in aqueous and micellar pseudophases, respectively.^{22,21}

The hydrolysis of triphenylphosphite was chosen because it is easy to follow the reaction photometrically and the reaction would not require use of buffers.

First, we studied the effect of micellized sulfonic acids on the hydrolysis of triphenylphosphite for comparison with the effect of sodium lauryl sulfate (NaLS) micelles on this reaction.

Second, we measured the effect of added sodium chloride, sodium bromide and tetramethylammonium bromide, and tetramethylammonium chloride upon the hydrolysis of triphenylphosphite in the presence of NaLS.

Third we studied the effect of cationic micelles of cetyltrimethylammonium chloride (CTACl) upon the reaction.



SCHEME II

RESULTS

Reactions in the Absence of Surfactant

Triphenylphosphite is not soluble in water so in order to obtain the first-order rate constant for the reaction of $(\text{PhO})_3\text{P}$ with H_2O in the presence of 0.05 M HCl. We followed the reaction in 50, 60, 70, 80 percent of H_2O in ethanol (v:v) and we calculate the first-order rate constant by extrapolation, and k'_w was $1.8 \times 10^{-4} \text{ s}^{-1}$. The acidity of the medium increases with the course of the reaction and this indicates that the product is an acid. It is well established that trialkylphosphite and triphenylphosphite give on hydrolysis in the presence of dilute acid the diester of phosphorous acid (A).^{39,40} In general, a hydroxy group bonded to trivalent phosphorus

$(\diagup \text{P}-\text{OH})$ is unstable, the stable structure being $(\text{H}-\text{P}=\text{O})$. For this reason, diesters of phosphorus acid such as (A) are unstable, and exist as diesters of phosphonic acid (B)³⁸ (Scheme I).

The reaction is first-order in $[\text{H}^+]$ in aqueous-organic solvent such as water and ethanol (Table V).

Reaction in the Presence of Surfactants

Since the surfactant is a solubilizing agent we have no problem of precipitation and we study the effects of both anionic micelles of NaLS and cationic micelles of CTACl.

The Effect of Anionic Micelle of NaLS

Anionic micelles of sodium lauryl sulfate (NaLS) modestly speed the reaction of triphenylphosphite with water in the presence of HCl. The observed first-order rate constant, k_{obs} , goes through maxima with increasing $[\text{NaLS}]$ (Figure 1).

Added electrolytes such as NaCl, NaBr, Me_4NCl , Me_4NBr slow reaction, as is general for reactions between oppositely charged ions. Sodium chloride and bromide have a similar effect and the tetramethylammonium chloride and bromide also have a similar effect (Table I). This similarity might be because the cation competing with H^+ is similar in each case. The rate of reaction continues to increase if we use constant $[\text{NaLS}]$ and increase $[\text{HCl}]$ (Table II).

The Effect of Micellized RSO_3H

The observed first-order rate constants k_{obs} continue to increase with increasing concentration of alkylhydrogensulfate (**2**) or alkyloxybenzenesulfonic acid **3b**, and it tends to reach a limiting value at high $[\text{RSO}_3\text{H}]$ (Figure 2).

The Effect of Cationic Micelles of CTACl

Cationic micelles of cetyltrimethylammonium chloride inhibit the reaction of triphenylphosphite in H_2O in the presence of 0.05 M HCl (Figure 1).

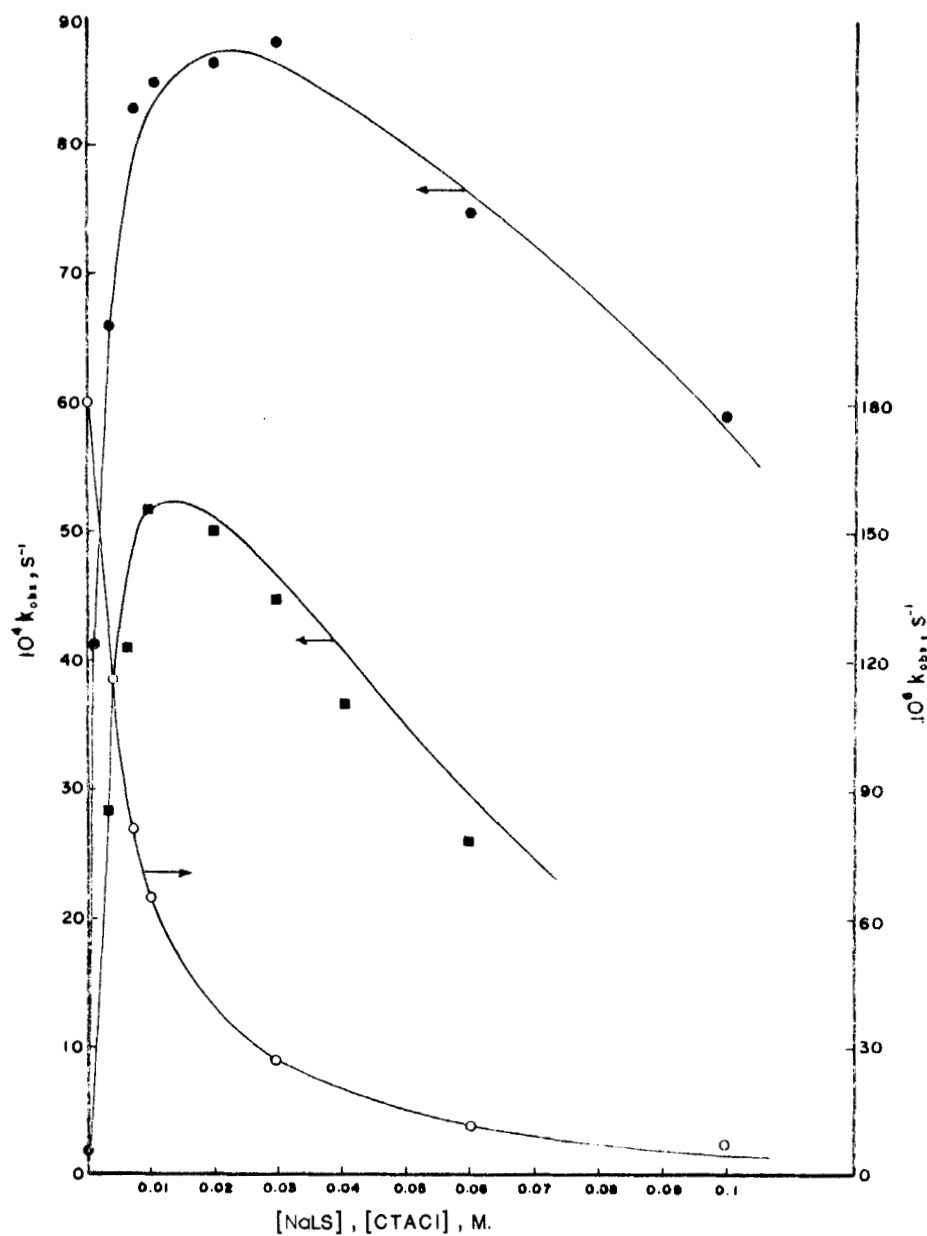


FIGURE 1 Hydrolysis of triphenylphosphite in anionic micelles of NaLS and cationic micelles of CTACl. In NaLS (■) 0.01 M HCl, (●) 0.05 M HCl. In CTACl (○) 0.05 M HCl.

TABLE I
Salt effects upon micellar catalysis^a

[Salt], M.	NaCl	Me ₄ NCl	NaBr	Me ₄ NBr
0.005	6.0(5.9)	6.2(6.2)	5.9(5.7)	6.1(6.2)
0.01	4.8(5.6)	5.2(5.8)	4.9(5.5)	5.5(5.9)
0.03	4.5(4.8)	5.1(5.2)	4.4(4.6)	5.0(5.2)
0.06	4.2(3.9)	4.8(4.7)	4.1(3.8)	4.8(4.7)
0.1	3.8(3.3)	4.6(4.3)	3.7(3.3)	4.6(4.3)
0.2	2.6(2.8)	4.4(4.0)	2.7(2.9)	4.3(3.9)

^a Values of $10^3 k_{\text{obs}} \text{ s}^{-1}$ at 25°C with 0.05 M HCl, 10^{-5} M substrate, and in the presence of 0.03 M NaLS. Values in parentheses are calculated.

TABLE II
The effect of [HCl] upon the first-order rate constant
at constant [NaLS]^a

$10^3 [\text{HCl}], \text{ M.}$	$10^4 k_{\text{obs}} \text{ s}^{-1}$
0.1	8.1 (9.0)
0.5	11.2 (12.3)
1	14.0 (15.0)
5	43.7 (42)
10	52.1 (52)
50	86.2 (89)
100	104 (100)

^a In the presence of 0.01 M NaLS. Values in parentheses are calculated.

DISCUSSION

Overall rate enhancements or inhibitions of bimolecular reactions by micelles, or similar colloids are due largely to the bringing together of the two reactants in the small volume of micelle or keeping them apart, respectively. We analyze our data using the ion exchange, pseudophase model although we recognize its imperfections and its failure at high concentrations of some ionic reagents.^{3,24-28}

Reactions in Anionic Micelles

Scheme I leads to Equation (1). The first-order rate constants

$$k_{\text{obs}} = k'_w + k'_M K_s [D_n] / (1 + K_s [D_n]) \quad (1)$$

are given by Equations (2) and (3). In Equation (3)

$$k'_w = k_w [H_w^+] \quad (2)$$

$$k'_M = k_M m_{\text{IH}}^s = k_M [H_M^+] / [D_n] \quad (3)$$

concentration of bound H^+ is written as a mole ratio.^{3,19,24a} We assume that H^+ and inert cation X^+ ($X = \text{Na}, \text{Me}_4\text{N}$) compete for the micelle according to Equation (4).^{3,24,29}

$$K_x^H = [H_w^+] [X_M^+] / [H_M^+] [X_w^+] \quad (4)$$

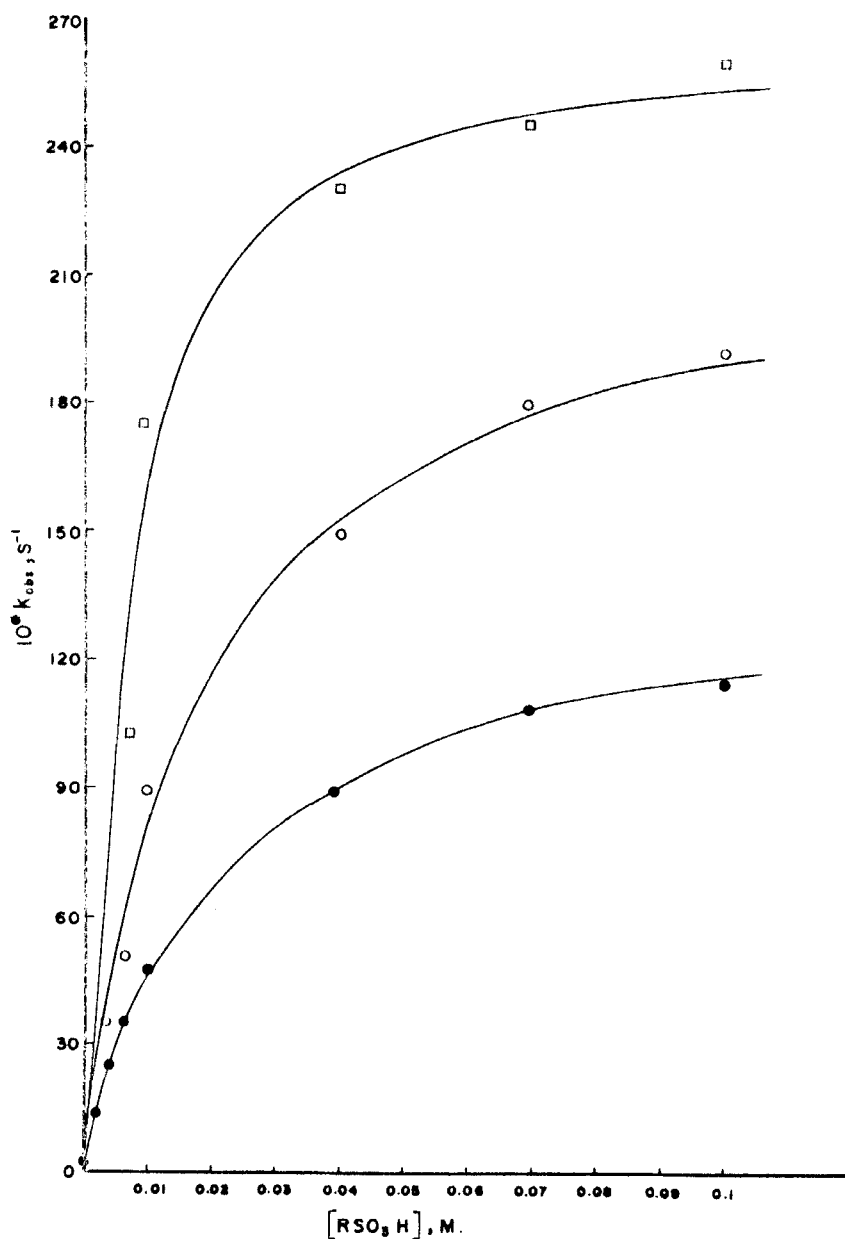


FIGURE 2 Hydrolysis of triphenylphosphite in alkylsulfonic acid micelles ($\bullet$) in $\text{C}_{12}\text{H}_{25}\text{OS}_3\text{H}$, ($\circ$) in $\text{C}_{14}\text{H}_{29}\text{SO}_3\text{H}$, ($\square$) in $p\text{-C}_{10}\text{H}_{12}\text{OC}_6\text{H}_4\text{-SO}_3\text{H}$.

The fraction of head groups neutralized by counterions, β , is given by $1-\alpha$, where α is the fractional ionization of the micelle. Equation (4), with the mass balance condition, gives m_H^s in terms of various parameters characteristic of the micelle, Equation (5).^{3,6,24}

$$(m_H^s)^2 + m_H^s \left(\frac{[H_T^+] + K_X^H[X_T^+]}{(K_X^H - 1)[D_n]} - \beta \right) - \frac{[H_T^+]\beta}{(K_X^H - 1)[D_n]} = 0 \quad (5)$$

Equations (1)–(5) can be used to calculate the rate-surfactant profiles^{6,19} for the reactions in the presence of NaLS and added salt or acid. Assumptions and approximations in this treatment have been discussed.³¹ In our calculations we use values of β from conductance data.¹⁴

In spite of some problems the pseudophase ion-exchange model gives reasonable fits of rate-surfactant-profiles and leads to consistent values of k_M , provided that high electrolyte concentrations are avoided and we apply it under these conditions (Figure 1 and Tables I and III).

For the reaction in absence of sodium cation, i.e., in reactive counterion micelles, we write the distribution of H^+ by using the mass-action-like Equation (6).

$$K'_H = [H_M^+]/\{[H_W^+][D_n] - [H_M^+]\} \quad (6)$$

The variation of k_{obs} with **2**, **3a**, and **3b** concentrations can be predicted by combining Equations (1), (2) and (6) by a computer program. This treatment has been

TABLE III
Fitting parameters for reaction of triphenylphosphite in NaLS micelles in the presence of 0.05 M HCl

Reaction medium	10^3 CMC, M	β	K_X^H	K_s, M^{-1}	$10^2 k_M, s^{-1}$	k_2^{ma}/k_w^b
NaLS	1.1	0.75	3	200	1.1	0.42
NaLS + NaCl	1.0	0.75	3	225	0.6	0.23
NaLS + NaBr	0.9	0.8	3	230	0.55	0.21
NaLS + Me ₄ NCl	0.7	0.75	8	230	0.66	0.26
NaLS + Me ₄ NBr	0.6	0.8	8	230	0.64	0.25

^a $k_2^m (M^{-1} s^{-1}) = 0.14 k_M (s^{-1})$; 0.14 M^{-1} is a conversion factor relating the rate constant expressed in terms of the mole ratio of H^+ per micellized surfactant head groups to that of H^+ per liter of Stern layer.

^b $k_w = 3.6 \times 10^{-3} M^{-1} S^{-1}$.

TABLE IV
Fitting parameters for reaction of triphenylphosphite in alkylsulfonic acid micelles

Surfactant	10^3 CMC, M	K'_H	K_s, M^{-1}	$10^2 k_M, s^{-1}$	k_2^{ma}/k_w^b
C ₁₂ H ₂₅ OSO ₃ H	1.5	100	220	1.2	0.47
C ₁₄ H ₂₉ SO ₃ H	1.78	100	250	2	0.77
p-C ₁₀ H ₂₁ OC ₆ H ₄ -SO ₃ H	4.5	100	270	2.8	1.1

^a $k_2^m (M^{-1} s^{-1}) = 0.14 k_M (s^{-1})$; 0.14 M^{-1} is a conversion factor relating the rate constant expressed in terms of the mole ratio of H^+ per micellized surfactant head groups to that of H^+ per liter of Stern layer.

^b $k_w = 3.6 \times 10^{-3} M^{-1} S^{-1}$.

applied successfully to reactions in micelles having OH^- , F^- , and HCO_2^- as counterions.^{6,7,30-32} The fitting parameters used to simulate our data are in Table IV.

The effect of HCl on k_{obs} , at constant surfactant concentration, was also calculated by using the same approach from values of k_s and k_M in Table III, assuming that the cmc remained constant,³⁴ Table II.

Reactions in Cationic Micelles

Cationic micelles of CTACl inhibit our reaction and that can be accounted for by solving Equation (1) and the approach is to rearrange it to Equation 7.⁹

$$\frac{1}{k_{\text{obs}} - k'_M} = \frac{1}{k'_w - k'_M} + \frac{1}{(k'_w - k'_M)K_s[D_n]} \quad (7)$$

However, the use of Equation 7 requires estimation of the concentrations of monomeric surfactant, which is often assumed to be that of the critical micelle concentration, cmc. Unfortunately the form of Equation 7 makes it very sensitive to the value of the cmc which is very sensitive to solutes especially hydrophobic substrate, and electrolyte (Table VI). Therefore the "kinetic" cmc is often taken as an adjustable parameter.¹⁷ To avoid this problem we can use the generalization that for many micellar-inhibited reactions $k'_w \geq k'_M$ ^{9,17,34} so that Equation 7 gives Equation 8^{24a} and we used Equation 8 to fit our data in the presence of CTACl. The value of k'_w was

$$k_{\text{obs}} = k'_w / (1 + K_s[D_n]) \quad (8)$$

TABLE V
The effect of [HCl] upon the first-order rate constants in
1:1 (v:v) water and ethanol^a

$10^3[\text{HCl}], \text{M}$	$10^4 k_{\text{obs}}, \text{S}^{-1}$
10	1.4
30	4.0
60	9.0
100	16.0
150	24.0
200	31.0

^a At 25.0° C with $5 \times 10^{-5} \text{ M}$ substrate.

TABLE VI
Acid and salt effect upon values of CMC of CTACl

$10^3[\text{HCl}], \text{M}$	Salt	$10^3 \text{ CMC}, \text{M}$
1.00		2.7
4.00		2.5
6.00		2.3
10.00		2.0
20.00		1.6
10.00	0.03 M Me_4NCl	1.0
10.00	0.10 M Me_4NCl	0.5
10.00	0.03 M NaCl	1.2
10.00	0.10 M NaCl	0.9

directly measured. The fits are illustrated in Figure 1 with values of $K_s = 200 \text{ M}^{-1}$ and $\text{cmc} = 1.2 \cdot 10^{-3} \text{ M}$.

Variations of Rate Constants with Surfactants

The simple distribution models fit the kinetic data reasonably well for the reactions in NaLS, RSO_3H and CTACl with parameters given in Tables III and IV as shown by the agreement between the experimental data and the theoretical calculations in Figures 1 and 2 and Tables I and II. Values of K_s increase slightly with increasing $[\text{HCl}]$ or $[\text{salt}]$. Calculations of k_M involve assumptions about such parameters as β , K_X^H , but k_M is insensitive to other than large changes in these parameters. The second order rate constants, k_M , have different dimensions from those of k_w [Equations (2) and (3)] but rate constants in the micelles can be compared with those in water provided that the micellar molar volume of reaction, V_M , is defined. Elsewhere we have taken $V_M = 0.14 \text{ L}$ so that we write a second-order rate constant, k_2^m , which can be compared with k_w .^{6,30} Hicks and Reinsborough have suggested that V_M varies with electrolyte concentration.³⁷

$$k_2^m = V_M k_M \quad (9)$$

Values of the second-order rate constant in NaLS k_2^m , $\text{M}^{-1}\text{s}^{-1}$ based on Equation (9) and (Tables III and IV) are slightly smaller than that in water and k_2^m and k_w are similar in alkylsulfonic acid micelles (Table IV).

Values of k_2^m/k_w are smaller in NaLS micelles and added salt than in alkylsulfonic acid micelles, which might be because NaLS micellizes better than those of alkylsulfonic acid. This behavior is general and suggests that the more hydrophobic substrates bind more deeply in the micellar surface farther away from bound H^+ . These differences suggest that the conversion factors of different micelles are not the same.

We do not know the dimensions of micelles of the sulfonic acids **2** and **3**, so that there is considerable uncertainty in the factor for the conversion of k_m to k_2^m , especially because it was estimated from dimensions of micelles of sodium lauryl sulfate. Our estimated volume of the stern layer is approximately half that of the micelle.

EXPERIMENTAL

Material. Triphenylphosphite (**1**) (Aldrich) was recrystallized before use. Surfactants such as CTACl and NaLS were synthesized or recrystallized by standard methods.^{6,12,19}

Dodecylhydrogensulfuric acid (2). The dried sodium lauryl sulfate (NaLS) was treated in dry Et_2O with HCl gas for 2 hours at low temperature (below 5°C) with vigorous stirring, formation of alkylhydrogensulfate (**2**) was slow and the process had to be repeated several times. The precipitate of NaCl was removed by filtration after the reaction was completed. The white (**2**) was recrystallized twice from hexane and dried under vacuum. The cmc by surface tension was $1.5 \times 10^{-3} \text{ M}$.

n-Tetradecansulfonic acid (3a). This compound was prepared using the procedure in Ref. 14. Surface tension measurements gave cmc values of $1.78 \times 10^{-3} \text{ M}$ (lit.^{14,23} 1.36×10^{-3} and $1.97 \times 10^{-3} \text{ M}$).

p-Decyloxybenzenesulfonic acid (3b). The recrystallized lead salt of p-hydroxybenzenesulfonic acid was refluxed with distilled n-dodecyl bromide (Aldrich) in H_2O -i-PrOH for 72 hrs. The lead salt of **3b** was isolated, recrystallized once from hot water, and extracted with dry Et_2O , removing a small amount

of oily material. The dried salt was treated in dry Et₂O with gaseous HCl for 40 min. with vigorous stirring. Formation of sulfonic acid was slow and the process had to be repeated several times. After complete reaction, the precipitate of PbCl₂ was removed by filtration.

The white **3b** was recrystallized twice from Et₂O-petroleum ether solution and dried under vacuum. The surfactant contained no Pb²⁺ as shown by addition of Na₂S. The surface tension had a small minimum. The calculated cmc estimated from surface tension was 4.5×10^{-3} M.

Kinetics. All reactions were followed spectrophotometrically by using a Perkin-Elmer spectrophotometer thermostated at $25.0 \pm 0.1^\circ\text{C}$. The hydrolysis of triphenylphosphite was followed at $\lambda_{\text{max}} = 270$ nm. Reactions were started by injecting 2–3 μl of 0.06 M triphenylphosphite in MeCN into 3 ml of surfactant solution giving final substrate concentration of Ca. 10^{-5} M. The first-order rate constants k_{obs} , are expressed in reciprocal seconds. We generally made 5–8 independent kinetic runs for each set of reaction conditions.

ACKNOWLEDGEMENT

This research (Chem 1409/14) was supported by the Research Center, College of Science, King Saud University, Riyadh, Saudi Arabia.

REFERENCES

1. D. G. Hall and B. A. Pethica, "Nonionic Surfactant," M. J. Shick and Marcell Dekker, Eds., New York, N.Y., 1967, p. 534.
2. P. Mukerjee, *Adv. Colloid Interface Sci.*, **1**, 241 (1967).
3. L. S. Romsted, "Surfactants in Solution," K. L. Mittal and B. Lindman, Eds. Plenum Press, New York, **2**, 1015 (1984).
4. A. D. Angeli, A. Cipiciani, R. Germani, G. Savelli, G. Cerichelli, and C. A. Bunton, *J. Colloid, Interface Sci.*, **121**, Jan. 1988.
5. D. Stigter, *J. Phys. Chem.*, **68**, 3603 (1964).
6. H. A. Al-Lohedan, C. A. Bunton, and L. S. Romsted, *J. Phys. Chem.*, **85**, 2123 (1981).
7. H. A. Al-Lohedan, *J. Chem. Soc. Perkin Trans.*, **2**, 1989.
8. P. Mukerjee in "Solution Chemistry of Surfactant," K. L. Mittal, Ed., Plenum Press, New York, **1**, 153 (1979).
9. F. M. Menger and C. E. Portnoy, *J. Am. Chem. Soc.*, **89**, 4698 (1967).
10. J. Buist, C. A. Bunton, L. Robinson, L. Sepulveda, and M. Stam, *J. Am. Chem. Soc.*, **92**, 4072 (1970).
11. E. J. Fendler, R. R. Liechti, and J. H. Fendler, *J. Org. Chem.*, **35**, 1658 (1970).
12. C. A. Bunton and B. Wolfe, *J. Am. Chem. Soc.*, **95**, 3742 (1973).
13. C. A. Bunton, K. Ohmenzetter, and L. Sepulveda, *J. Phys. Chem.*, **81**, 2000 (1977).
14. C. A. Bunton, L. S. Romsted, and G. Savelli, *J. Am. Chem. Soc.*, **101**, 1253 (1979).
15. C. A. Bunton and M. J. Minch, *Tetrahedron Lett.*, 3881 (1970); C. A. Bunton, A. Kamego, and M. J. Minch, *J. Org. Chem.*, **37**, 1388 (1972).
16. E. J. Cordes and R. B. Dunlap, *Acc. Chem. Res.*, **2**, 329 (1969).
17. J. H. Fendler and E. J. Fendler, "Catalysis in Micellar and Macromolecular Solutions," Academic Press, New York, N.Y., 1975.
18. C. A. Bunton and M. J. Minch, *J. Phys. Chem.*, **78**, 1490 (1974).
19. H. A. Al-Lohedan, C. A. Bunton, and L. S. Romsted, *J. Org. Chem.*, **47**, 3528 (1982).
20. A. P. Osipov, K. Martinek, A. K. Yatsimirsiki, and I. V. Berezin, *Akad. Nauk SSSR, Ser. Khim.*, 1984, 1974; S. J. Dougherty and J. G. Berg, *J. Colloid Interface Sci.*, **49**, 135 (1974).
21. H. A. Al-Lohedan, *J. Phys. Chem.*, **91**, 4524 (1987).
22. C. A. Bunton, L. S. Romsted, and G. Savelli, *J. Am. Chem. Soc.*, **101**, 1253 (1979).
23. J. K. Weil, F. D. Smith, A. J. Stirton, and R. G. Bistline, Jr., *J. Am. Oil. Chem. Soc.*, **40**, 538 (1963).
24. C. A. Bunton, *Catal. Rev. Sci. Eng.*, **20**, 1 (1979); (b) E. J. R. Sudholter, G. B. Van de Langkruis, and J. B. F. N. Engberts, *Rec. Trav. Chem. Pays-Bas*, **99**, 73 (1980).
25. T. J. Broxton and D. B. Sango, *Aust. J. Chem.*, **36**, 711 (1983); T. J. Broxton, *Ibid.*, **34**, 2313 (1981).
26. A. Cipiciani, R. Germani, G. Savelli, and C. A. Bunton, *Tetrahedron Lett.*, **25**, 3765 (1984).
27. N. B. Gersmantel and M. I. Page, *J. Chem. Soc., Perkin Trans. 2*, **147**, 155 (1982).
28. F. Nome, A. F. Rubira, C. Franco, and L. G. Ionescu, *J. Phys. Chem.*, **86**, 1881 (1982); M. Gonsalves, S. Probst, M. C. Rezende, F. Nome, C. Zucco, and D. Zanette, *ibid.*, **89**, 1127 (1985).

29. L. S. Romsted, in "Micellization Solubilization and Microemulsions," K. L. Mittal, Ed., Plenum Press, New York, **2**, 509 (1977).
30. C. A. Bunton, L. H. Gan, J. R. Moffatt, L. S. Romsted, and G. Savelli, *J. Phys. Chem.*, **85**, 4118 (1981).
31. H. A. Al-Lohedan, *Asian J. Chem.*, **3**, 323 (1991).
32. H. A. Al-Lohedan and C. A. Bunton, *J. Org. Chem.*, **7**, 1160 (1982).
33. In this treatment we neglect the electrolyte effect of HCl on the cmc.
34. F. H. Quina, M. J. Politi, I. M. Cuccovia, S. M. Martins-Franchetti, and H. Chaimovich, "Solution Behavior of Surfactants," K. L. Mittal and E. J. Fendler, Eds. Plenum Press, New York, **11**, 1125 (1982).
35. L. M. Cuccovia, F. H. Quina, and H. Chaimovich, *Tetrahedron*, **38**, 917 (1982).
36. H. A. Al-Lohedan, *J. Phys. Chem.*, **94**, 8226 (1990).
37. J. R. Hicks and V. C. Reinsborough, *Aust. J. Chem.*, **35**, 15 (1982).
38. J. O. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry," W. A. Benjamin, Inc., 1202 (1964).
39. I. L. Finar, "Organic Chemistry," The Fundamental Principles, sixth edition, Longman Group Limited, **1**, 412 (1973).
40. A. D. F. Toy, "Phosphorus Chemistry in Everyday Living," second printing, American Chemical Society, 150 (1977).