

Kinetics of the Reversible Hydration of 1,3-Dichloroacetone catalysed by Micellar Aerosol-OT in Carbon Tetrachloride

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The kinetics of the reversible hydration of 1,3-dichloroacetone (DCA) by Aerosol-OT (AOT) solubilized water or D₂O, have been studied in carbon tetrachloride. In the presence of the surfactant, rate constants for hydration or dehydration are faster than those in water-dioxan and/or D₂O-dioxan mixtures. Rate enhancements range from 1 808 to 111 for hydration by water-AOT, and from 1 619 to 124 for hydration by D₂O-AOT. The corresponding ratios for the dehydration reaction range from 508 to 64 and 1 788 to 104 for water-AOT and D₂O-AOT, respectively. Equilibrium constants for hydration are also higher in the presence of AOT than those in water- or D₂O-dioxan mixtures. The results are discussed in terms of the unique properties of AOT solubilized water, as well as participation of the surfactant head-groups in the slow water attack.

THE study of the catalytic effect of micelles on reaction rates is a subject of increasing interest.¹⁻³ As catalysts, surfactants present several advantages, they are inexpensive, commercially available, and their structure can be easily modified (for example by quaternization, *etc.*) according to the researcher's need. On the other hand, micellar catalysis has been used as a simple model for more complex enzymatic reactions.¹⁻³

Several detergents, *e.g.* bis-2-ethylhexyl sodium sulphosuccinate, Aerosol-OT (AOT) [C₈H₁₇OCO-CH₂-C(SO₃⁻

Na⁺)H-COOC₈H₁₇] aggregate in organic solvents,^{4,5} and these aggregates enhance the rates of many reactions, sometimes dramatically.^{6,7} Rate enhancement by aqueous micelles has been explained in terms of electrostatic and hydrophobic factors.^{1,2} In non-aqueous solvents the rate increase can be the result of the change in the reactivity of substrates, and of solubilized water,

⁴ O. A. El Seoud, E. J. Fendler, J. H. Fendler, and R. T. Medary, *J. Phys. Chem.*, 1973, **77**, 1876; E. J. Fendler, V. Constein, and J. H. Fendler, *ibid.*, 1975, **79**, 917.

⁵ J. B. Peri, *J. Colloid Interface Sci.*, 1969, **29**, 6; K. Kon-No and A. Kitahara, *ibid.*, 1971, **35**, 636.

⁶ J. H. Fendler, *Accounts Chem. Res.*, 1976, **9**, 153.

⁷ O. A. El Seoud, *J.C.S. Perkin II*, 1976, 1497.

¹ E. H. Cordes and C. Gitler, *Bio-org. Chem.*, 1973, **2**, 1.

² C. A. Bunton, *Progr. Solid State Chem.*, 1973, **8**, 239.

³ J. H. Fendler and E. J. Fendler, 'Catalysis in Micellar and Macromolecular Systems', Academic Press, New York, 1975.

when they are solubilized inside the micelle, and also through participation of the surfactant head-groups.^{8,9}

It has been recently shown that the non-ionic detergent Triton X-100 increases the rate of hydration of acetaldehyde in carbon tetrachloride.⁷ We report here a study on the effects of AOT on the hydration of 1,3-dichloroacetone (DCA) in carbon tetrachloride. This is one of the few studies,¹⁻³ in which the effect of a detergent on both rate and equilibrium constants of a reaction has been investigated.

EXPERIMENTAL

Carbon tetrachloride (Merck; Uvasol; maximum water content 0.005%) was further dried by storing over activated 4A molecular sieve for several weeks. Dioxan (Aldrich; Gold Label) was refluxed, then distilled from sodium. The solvent was stored in the dark and used within a week. DCA (Eastman Kodak) was purified by two vacuum distillations. The ketone had molar absorptivity 41.1 ± 0.1 at 298 nm in carbon tetrachloride, which is in good agreement with the values reported elsewhere.¹⁰ No hydrate or any other impurity was detected in the ¹H n.m.r. spectrum of a 0.6M solution of the ketone in carbon tetrachloride, immediately after preparation or after several days. AOT (Aldrich; 96%) was purified as before.¹¹ Deuterium oxide (Stohler Isotope Chemicals; 100% D) and doubly distilled water were used throughout.

¹H N.m.r. spectra were obtained on a Varian XL-100 spectrometer (100 MHz) equipped with a frequency counter and operating at $33 \pm 0.5^\circ$. Chemical shifts were measured at 500 Hz sweep width and are given on the δ scale relative to internal tetramethylsilane; they are accurate to ± 0.1 Hz.

Special care was taken to exclude moisture during all stock solution preparations and manipulation. The reagent stock solutions in carbon tetrachloride were; AOT 1.0M and DCA 0.6M. The surfactant was weighed, dried *in vacuo* (ca. 0.05 Torr) over P₂O₅ for at least 12 h, and reweighed before making up the stock solution. The latter was renewed daily, that of DCA was renewed weekly.

Kinetic measurements were carried out spectrophotometrically using a Zeiss PMQ II spectrometer equipped with a thermostatted cell holder. The temperature was controlled inside the reaction cell to $\pm 0.05^\circ$. Kinetic runs were carried out as follows. The required amounts of water, or D₂O, were added to AOT solution (0.8 ml) contained in a tightly stoppered quartz cell and the solution shaken till clear. The required volume of carbon tetrachloride was added, the solution shaken, and the cell placed in the spectrometer cell holder. The reaction was started by pipetting the DCA stock solution (0.1 ml) which was kept at 25°. The equilibrium and kinetics of hydration were investigated by observing the change in the carbonyl group absorption at 316 nm.* The absorbance (A_t) decreased until equilibrium was reached, and the equilibrium reading (A_e) was constant for several hours.

Observed rate constants k_{obs} were evaluated from \ln

* Due to the absorption of AOT at this wavelength, the reference cell contained 0.5M-AOT solution.

† Both the correlation coefficient and the standard deviation indicated excellent fit of the data to a straight line.

⁸ J. H. Fendler, E. J. Fendler, R. T. Medary, and V. A. Woods, *J. Amer. Chem. Soc.*, 1972, **94**, 7288; J. H. Fendler, E. J. Fendler, and S. A. Chang, *ibid.*, 1973, **95**, 3273; C. J. O'Connor, E. J. Fendler, and J. H. Fendler, *J. Org. Chem.*, 1973, **38**, 3371.

($A_t - A_e$) against t using a Hewlett-Packard model 9820A programmable calculator.†

Since the concentration of water remains effectively constant during each experiment, the reaction can be characterized by two first-order rate constants k_h and k_d for hydration and dehydration respectively. At constant water concentration, the equilibrium constant for hydration K_h and the observed rate constant k_{obs} are given by equations (1) and (2). Values of K_h , k_h , and k_d can be easily

$$K_h = \frac{[(\text{CH}_2\text{Cl})_2\text{C}(\text{OH})_2]}{[(\text{CH}_2\text{Cl})_2\text{C}=\text{O}]} = k_h/k_d \quad (1)$$

$$k_{\text{obs}} = k_h + k_d \quad (2)$$

determined by equations (3) and (4)¹⁰ where A_o is the

$$K_h = (A_o - A_e)/A_e \quad (3)$$

$$k_h = k_{\text{obs}}(A_o - A_e)/A_o \quad (4a)$$

$$k_d = k_{\text{obs}}A_e/A_o \quad (4b)$$

absorbance at $t = 0$, obtained by adding the value of A_e to the intercept of the graph between $\ln(A_t - A_e)$ and t : A_t and A_e are as defined before.

RESULTS

Our results for hydration in water-dioxan mixtures, at water concentrations of 2.04, 2.64, 3.06, and 3.31M, are in

TABLE 1

Data for the hydration in presence of H₂O-0.4M-AOT in carbon tetrachloride at 25°

[Water]/M	$10^4 \times k_h/s^{-1}$	$10^4 \times k_d/s^{-1}$	K_h
0.278	5.7	10.4	0.548
0.555	9.4(1808)	13.2(508)	0.712(3.568)
0.833	13.1(728)	16.5(266)	0.794(2.743)
1.111	18.8(470)	19.7(188)	0.954(2.503)
1.389	23.6(158)	23.7(158)	0.996(2.135)
1.667	28.4(249)	27.9(140)	1.018(1.786)
1.944	36.7(212)	33.0(124)	1.112(1.716)
2.222	44.6(178)	38.1(106)	1.171(1.687)
2.50	48.7(139)	41.3(86)	1.179(1.617)
2.778	58.6(126)	48.0(77)	1.221(1.628)
3.055	65.4(111)	50.4(65)	1.298(1.717)
3.333	83.1(113)	62.4(64)	1.331(1.756)

TABLE 2

Rate and equilibrium constants for the hydration in presence of D₂O-0.4M-AOT in carbon tetrachloride at 25°

[D ₂ O]/M	$10^4 \times k_h/s^{-1}$	$10^4 \times k_d/s^{-1}$	K_h
0.25	3.4(1619)	5.9(1788)	0.576(0.906)
0.50	5.0(1389)	6.5(970)	0.769(1.432)
0.75	6.5(1083)	7.2(576)	0.903(1.881)
1.0	8.0(800)	8.5(425)	0.941(1.882)
1.25	9.9(572)	9.5(317)	1.042(1.806)
1.50	12.4(413)	10.6(247)	1.170(1.676)
1.75	15.1(315)	11.8(197)	1.279(1.599)
2.0	17.1(238)	12.8(158)	1.336(1.503)
2.25	19.9(199)	14.7(143)	1.354(1.394)
2.50	22.8(170)	16.0(126)	1.425(1.351)
2.75	25.0(146)	17.2(114)	1.453(1.284)
3.0	27.9(128)	18.7(105)	1.492(1.218)
3.25	30.8(124)	20.2(104)	1.525(1.200)

good agreement with those reported by Bell *et al.*¹² Rates and equilibrium constants for the hydration of DCA in the

⁹ O. A. El Seoud, A. Martins, L. P. Barbur, M. J. Da Silva, and V. Aldridge, *J.C.S. Perkin II*, 1977, 1674.

¹⁰ R. P. Bell and J. E. Critchlow, *Proc. Roy. Soc.*, 1971, **A325**, 35.

¹¹ O. A. El Seoud and J. H. Fendler, *J.C.S. Faraday I*, 1975, 452.

¹² R. P. Bell, J. P. Millington, and J. M. Pink, *Proc. Roy. Soc.*, 1968, **A303**, 1.

presence of 0.4M-AOT are listed in Tables 1 and 2. The figures in parentheses refer to the ratios of the rate or equilibrium constants (water-AOT or D₂O-AOT) to those in water- or D₂O-dioxan. The latter constants were obtained from plots of log *k* against [water] or [D₂O], using the data of Bell *et al.*¹² Rate constants in the presence of AOT were always higher than the corresponding values in water- or D₂O-dioxan. The rate ratios decrease with increasing water or D₂O concentration, becoming constant as the saturation point of the surfactant (by water or D₂O) is approached. Equilibrium constant ratios for water-AOT follow a similar pattern, whereas those for D₂O-AOT exhibit an initial increase followed by a gradual decrease at higher D₂O concentrations.

The kinetic orders with respect to water ($n_h^{H_2O}, n_d^{H_2O}$) and D₂O ($n_h^{D_2O}, n_d^{D_2O}$) were obtained from the slopes of graphs of log *k_h* or log *k_d* against log [water] or [D₂O], respectively. Each graph consisted of two intersecting straight lines, so that the values of *n* depend on the water concentration range. In both cases the two lines intersected at *ca.* 1.0M-water or -D₂O, and the slopes at the lower water concentrations were less than those at concentrations >1.0M. The values were: 0.76, 1.26 ($n_h^{H_2O}$); 0.41, 0.96 ($n_d^{H_2O}$); 0.58, 1.15 ($n_h^{D_2O}$); 0.19, 0.95 ($n_d^{D_2O}$) respectively.

The kinetic isotope effect for hydration $k_h^{H_2O}/k_h^{D_2O}$ increases gradually as a function of water concentration up to *ca.* 2.0M; above this concentration, the increase is more pronounced. The ratio of $k_d^{H_2O}:k_d^{D_2O}$ increases smoothly over the whole concentration range.

TABLE 3

Effect of increasing AOT concentration on DCA hydration ^{a, b}

[AOT]/M	10 ⁴ × <i>k_h</i> /s ⁻¹	10 ⁴ × <i>k_d</i> /s ⁻¹	<i>K_h</i>
0.15	35.6	64.1	0.555
0.20	35.0	55.1	0.635
0.25	32.8	48.1	0.682
0.30	30.7	38.0	0.808
0.35	27.7	33.7	0.822
0.40	24.3	24.8	0.980

^a In carbon tetrachloride at 25°. ^b Water concentration was kept constant at 1.50M.

At a constant water concentration (1.5M), *k_h* and *k_d* increase, whereas *K_h* decreases as a function of decreasing AOT concentration as shown in Table 3.

DISCUSSION

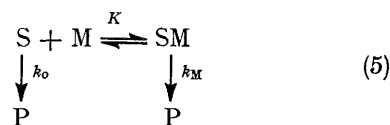
In non-aqueous solvents, AOT aggregates so that the polar head groups are packed around a micellar core, whereas the hydrophobic tails are in contact with the solvent.⁵ Because of the very low solubility of water in carbon tetrachloride, AOT solubilized water concentrates in the micellar core, in form of an aqueous 'pool' surrounded by the AOT head groups.¹³

* The solvent used was 30% v/v C₆D₆ in carbon tetrachloride. The micellar concentration [M] was calculated using the equation $[M] = (C_D - c.m.c.)/N$, where *C_D* is the total detergent concentration and *N* its aggregation number.⁹ Values of the critical micelle concentration, c.m.c., and *N* were taken from refs. 5 and 15.

† At 25° the distribution coefficient of DCA $\alpha = [DCA \text{ in } CCl_4]/[DCA \text{ in water}] = 0.49$.

¹³ K. Kon-No and A. Kitahara, *J. Colloid Interface Sci.*, 1971, **35**, 409; F. M. Menger, G. Saito, G. V. Sanzero, and J. R. Dodd, *J. Amer. Chem. Soc.*, 1975, **97**, 909.

Micellar catalysis can be represented by equation (5)¹⁻³ where S, M, and SM represent substrate, micelle,



and substrate-micelle complex respectively, *k_o* and *k_M* are rate constants for the reaction in the bulk solvent and in the micelle, and *K* is the substrate-micelle association constant. The latter can be determined from the chemical shifts of the DCA methylene protons as a function of increasing AOT concentration according to equation (6).¹⁴ Here Δ is the difference between the

$$\Delta/[M] = -\Delta K + \Delta_c K \quad (6)$$

observed chemical shift and that of the uncomplexed or 'free' DCA, and Δ_c is the difference between the chemical shift of the micelle-complexed and that of the uncomplexed substrate, [M] is the surfactant micellar concentration.* The value of *K* was found to be $37.3 \pm 1 \text{ l mol}^{-1}$ which means that in a solution of 0.03M-DCA and 0.4M-AOT (corresponding to 0.019M-micelle) *ca.* 57% of the ketone will be in the micellar core. This fraction is expected to increase in the presence of solubilized water because DCA is more soluble in water than in carbon tetrachloride.† Additionally, the rate of hydration of DCA in water-saturated carbon tetrachloride is negligible. This means that the ketone partitions in favour of, and hydrates in, the micellar water 'pool'.

Attention is now focused on the kinetics of the hydration reaction in the presence of AOT, and the catalytic role of the latter. An important factor in explaining the observed catalysis is the change in the properties of water when it is solubilized in the micellar 'core'. For example it has been shown that both macroscopic and microscopic polarities of AOT solubilized water are quite different from those in bulk water.^{13,16,17} This has an obvious implication for the observed rate since water is one of the reactants. The enhanced reactivity of water solubilized by reversed micelles has been used to explain the rate increase for several reactions involving water as a reactant.^{7,18}

The kinetic isotope effect, and its variation as a function of increasing water or D₂O concentration, is more or less similar to that observed in water-dioxan.¹² The transition state (7) is suggested for the latter case¹⁰ and involves the participation of two extra water

¹⁴ R. Foster and C. A. Fyfe, *Trans. Faraday Soc.*, 1965, **61**, 1626; W. R. Carper, C. M. Buess, and G. R. Hipp, *J. Phys. Chem.*, 1970, **74**, 4229.

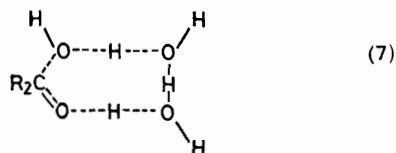
¹⁵ S. Muto and K. Meguro, *Bull. Chem. Soc. Japan*, 1973, **46**, 1316.

¹⁶ F. M. Menger, J. A. Donohue, and R. F. Williams, *J. Amer. Chem. Soc.*, 1973, **95**, 4931.

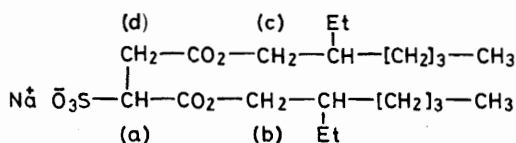
¹⁷ M. Wong, J. K. Thomas, and M. Grätzel, *J. Amer. Chem. Soc.*, 1976, **98**, 2391.

¹⁸ C. J. O'Connor, E. J. Fendler, and J. H. Fendler, *J. Amer. Chem. Soc.*, 1973, **95**, 600; *J.C.S. Dalton*, 1974, 625.

molecules, in addition to the one reacting.^{10,*} A transition state similar to (7) can be written for the AOT catalysed hydration, in which the surfactant



replaces one, or two, of the water molecules. It is possible that the sulphonate group acts as a general base for the slow attack of water. Evidence for the presence of strong interaction between the surfactant head-groups and solubilized water comes from the upfield shift of the water n.m.r. signal,¹⁹ as well as from the shifts of the discrete protons of the surfactant. Proton



(a) appears as a sharp triplet, protons (b)—(d) as doublets, and all other protons as two broad singlets. Table 4 shows the variation of the chemical shifts of protons (a)—(d) as a function of added D₂O. Only H(a) and H(d) shift appreciably upfield on adding water, with $\Delta\delta(\text{a}) \text{ ca. } 3\Delta\delta(\text{d})$. Table 4 shows clearly the strong

TABLE 4

Chemical shifts of some AOT protons as a function of D₂O concentration^a

[D ₂ O]/M	$\Delta\delta(\text{a})/\text{Hz}^b$	$\Delta\delta(\text{b})/\text{Hz}$	$\Delta\delta(\text{c})/\text{Hz}$	$\Delta\delta(\text{d})/\text{Hz}$
0.50	-6.0	-1.2	-0.3	-1.2
1.0	-10.3	-1.6	-0.2	-3.2
1.50	-13.1	-1.6	0.1	-4.2
2.0	-14.8	-1.3	0.7	-4.6
2.50	-15.2	-1.3	0.9	-5.2
3.0	-16.6	-1.3	1.4	-5.4

^a Conditions: AOT, 0.4M; solvent 30% v/v C₆H₆ in carbon tetrachloride; *T* 33°. ^b $\Delta\delta$ = Chemical shift in presence of D₂O - chemical shift in its absence. Initial chemical shifts were δ 4.496 (a), 4.173 (b), 3.974 (c), and 3.313 (d).

hydration of the AOT head groups. The results for H(b) and H(c) leave in doubt whether the ester groups come in contact with the water pool. The shifts of H(a) and H(d) can be explained as follows: any interaction between the head-groups (SO₃⁻ and Na⁺ ions) with water will be at the expense of their strong mutual interaction. As a result of hydration, the charge neutralization decreases and H(a) and H(d) shift upfield, due to electronic effects and/or diamagnetic shielding.

* Transition state (7) is drawn with the protons symmetrically placed between two oxygen atoms, but this does not imply any particular degree of proton transfer.

¹⁹ S. G. Frank, Y. H. Shaw, and N. C. Li, *J. Phys. Chem.*, 1973, **77**, 239.

²⁰ M. B. Mathews and E. J. Hirschhorn, *J. Colloid Sci.*, 1952, **8**, 86.

The apparent kinetic orders with respect to water and D₂O throw some light on the participation of AOT in the catalysis. In water-dioxan, both $n_{\text{H}_2\text{O}}$ and $n_{\text{D}_2\text{O}}$ are ca. 3, whereas $n_{\text{d}^{\text{H}_2\text{O}}}$ and $n_{\text{d}^{\text{D}_2\text{O}}}$ are ca. 2, as required by transition state (7). The observed n values in the presence of AOT depend upon the concentration range of water and have a maximum value of ca. 1. Actually n represents the increase in hydration in going from reactants to the transition state. A value <3 implies the participation of a catalyst.¹⁰ The maximum value of n does not necessarily mean, however, that AOT replaced two water molecules in the transition state, because one has to consider the surfactant hydration in the initial state. The dependence of n_{h} and n_{d} on water concentration may reflect different degrees of surfactant hydration. In other words, the first added water is bound strongly in a primary hydration shell, followed by a secondary shell of less bound water.^{13,17,20,21} It is reasonable that the structure, hence the properties, of the micelle solubilized water is different in the two hydration shells, which explains the different values of n . A parallel line of reasoning was used to explain the dependence of n on the water concentration range in the solvolysis of organic halides and sulphonates in water-acetone and water-dioxan.²²

The data of Table 3 are in agreement with the above conclusions. At a fixed water concentration, both k_{h} and k_{d} decrease as a function of increasing AOT concentration. This is because the higher the surfactant

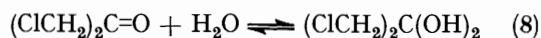
TABLE 5

Isotope effects in equimolar water-D₂O mixtures^{a,b}

[Water-D ₂ O]/M	$k_{\text{h}^{\text{D}_2\text{O}}}/k_{\text{h}^{\text{H}_2\text{O}}}$	Observed $k_{\text{h}^{\text{D-H}}}/k_{\text{h}^{\text{H}_2\text{O}}}$	Calculated $k_{\text{h}^{\text{D-H}}}/k_{\text{h}^{\text{H}_2\text{O}}}$		
			<i>m</i> 2	<i>m</i> 4	<i>m</i> 6
0.50	0.588	0.774	0.780	0.773	0.772
0.75	0.549	0.745	0.758	0.749	0.746
1.0	0.515	0.730	0.737	0.727	0.724
1.50	0.510	0.735	0.734	0.724	0.721
2.0	0.481	0.701	0.717	0.705	0.701
2.50	0.469	0.695	0.710	0.697	0.693

^a In the presence of 0.4M-AOT, *T* 25°. ^b In all cases, the correlation coefficient of the $\ln(A_t - A_e) - t$ graphs was >0.999, and the percentage relative standard deviation (standard deviation $\times 100$)/ k_{obs} was <2%.

concentration, the more water is involved in the hydration shell and the slower is the reaction. On the other hand, K_{h} increases as a function of increasing AOT concentration probably because in equilibrium (8) the



sulphonate group (acting as a general base) can form a

²¹ H. F. Eicke and J. C. W. Shepherd, *Helv. Chim. Acta*, 1974, **51**, 1951; H. Christen, H. F. Eicke, H. Hammerich, and U. Strahm, *ibid.*, 1976, **59**, 1297.

²² E. Tommila, M. Tiilikainen, and A. Voipio, *Ann. Acad. Sci. Fennicae*, 1955, AII, 65; *Acta Chem. Scand.*, 1955, **9**, 975; E. Tommila, E. Paakkala, U. K. Virtanen, A. Erva, and S. Varila, *Ann. Acad. Sci. Fennicae*, 1959, AII, 91.

stronger hydrogen bond with the hydrate (pK_a 11.6),²³ than with the attacking water.

It is possible to probe the structure of the transition state by applying the fractionation factor theory,²⁴ to the results of hydration by equimolar mixtures of water and D_2O (Table 5). The fractionation factor ϕ for a given exchangeable site, describes the equilibrium isotope composition at that site, with respect to the isotope composition of the solvent. The kinetic solvent isotope effect is given by equations (9) and (10), where

$$k^{D_2O}/k^{H_2O} = \prod_i \phi_{\ddagger} / \prod_i \phi_i \quad (9)$$

$$\frac{k^{D-H}}{k^{H_2O}} = \frac{\prod_{\ddagger}(1-x+x\phi_{\ddagger})}{\prod_i(1-x+x\phi_i)} \quad (10)$$

k^{D_2O} , k^{H_2O} , and k^{D-H} refer to rate constants in D_2O , water, and in water- D_2O , respectively, x is the atom fraction of D in the solvent, and the subscripts i and \ddagger refer to initial and transition states respectively. 1H N.m.r. spectra showed that there was no hydrogen exchange between DCA and AOT solubilized D_2O . The only exchangeable hydrogens in the initial state are, therefore,

²³ J. E. Critchlow, *J.C.S. Faraday I*, 1972, 1774.

²⁴ V. Gold, *Adv. Phys. Org. Chem.*, 1969, **7**, 259; J. Albery, 'Proton-Transfer Reaction', eds. E. Caldin and V. Gold, Chapman and Hall, London, 1975.

those of water for which $\phi = 1$ ²⁴ so that equations (9) and (10) can be rewritten as (11) and (12) where m is the number of exchangeable protons in the transition state.* From $k_h^{D_2O}$ and $k_h^{H_2O}$ one can calculate values of ϕ_{\ddagger} for $m = 2, 4$, and 6 .^{10,24} These values are then used

$$k_h^{D_2O}/k_h^{H_2O} = \prod_1^m \phi_{\ddagger} \quad (11)$$

$$k_h^{D-H}/k_h^{H_2O} = \prod_1^m (1-x+x\phi_{\ddagger}) \quad (12)$$

to calculate the ratio $k_h^{D-H}/k_h^{H_2O}$ and the calculated ratios compared with the experimental ones as given in Table 5. The results show that a two-proton transition state can be excluded. A four-proton transition state seems to fit the data best, in agreement with the idea that AOT replaces one water molecule.

The above discussion illustrates that in explaining reversed micellar catalysis, one has to consider the difference of substrate reactivities between the micellar core and bulk solvent, as well as the possible participation of the surfactant head-groups.

[7/1123 Received, 28th June, 1977]

* The maximum value of m , *i.e.*, that for transition state (7) is 6; the minimum value, *i.e.*, when no extra water molecules participate is 2.