Hydrolysis of Phenylureas. Part III.[1] Micellar Effects on the Solubilization and Decomposition of 4-Methyl- and 4-Nitro-phenylurea

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Measurement of the critical micelle concentration of non-ionic nonylphenoxypoly(oxyethylene)-14-ethanol (A-730) and cationic hexadecyltrimethylammonium bromide (CTAB) by surface tension and u.v. spectroscopic methods shows large increases on addition of very small amounts of 4-methyl- and 4-nitro-phenylureas. Micellar A-730, CTAB, and anionic sodium dodecyl sulphate (NaLS) have little effect on the rate constants of hydrolysis of these ureas. Arrhenius parameters have been evaluated and the mechanisms of hydrolysis are discussed in terms of sites of solubilization. By contrast, dodecylammonium propionate (DAP) in benzene enhances the rate of decomposition of 4-nitrophenylureas 3 × 10^3 fold. This observed catalysis is discussed in terms of solubilization of the substrate in the polar micellar cavity where it is held fairly rigidly, thus enhancing proton transfer. General-acid and -base catalysis is also observed in DAP.

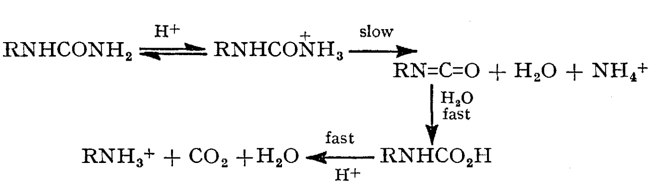
RATES of hydrolysis of 4-methyl- (I) and 4-nitro-phenylurea (II) have been determined recently[2] at pH 0—14 at 101°. The profiles of k_ψ against pH showed plateaux between pH 6.80 and 8.10 for (I) and between 6.24 and 8.01 for (II), and there is evidence for general acid and general base catalysis.

We have examined the effects of cationic micellar hexadecyltrimethylammonium bromide (CTAB), anionic sodium dodecyl sulphate (NaLS), and nonionic nonylphenoxypoly(oxyethylene)-14-ethanol [Antarox CO-730 (A-730) or Igepal CO-730] on the rates of hydrolysis of (I) and (II) in the plateau region of pH and also in acidic and basic media. The minimal catalysis observed has been interpreted in terms of sites of solubilization as shown by n.m.r. and u.v. spectroscopy.

$NH_2C(=O)NHC_6H_4R$

(I) R = 4-Me
(II) R = 4-NO_2

By contrast dramatic rate enhancement for decomposition of (II) was obtained by use of reversed micellar dodecylammonium propionate (DAP) in benzene. The reaction we are studying is shown in the Scheme.



SCHEME

Thus in acid solution the product of hydrolysis is the protonated aniline,[1,3] in basic solution the carbamic acid in equilibrium with the corresponding aniline,[2] and in non-aqueous solvents containing a detergent with proton-donating powers the decomposition product is the phenyl isocyanate.

Marked decreases in micellization tendencies have been found for A-730 and CTAB on addition of trace amounts of (I) and (II). Such decreases have previously been found only on addition of molar quantities of urea (Table 1).

EXPERIMENTAL

Materials.—The preparation of (I) [3] and (II) [1] has been described. Doubly distilled deionised water was used for the preparation of the buffer and surfactant solutions. AnalaR benzene (<0.02% water) was distilled from sodium onto freshly activated Linde type 5A molecular sieve and stored under nitrogen.

A-730 (G.A.F. Corporation) was used without further purification. CTAB (Eastman-Kodak) was purified by the method of Duynstee and Grunwald [4] and NaLS (B.D.H.) by the method of Mukerjee and Mysels.[5] DAP, m.p. 55.0°, was prepared by the method of Kitahara.[6]

Measurement of Rate Constants of Hydrolysis.—The procedure for aqueous micellar solutions is similar to that already described.[1,3] Rates of hydrolysis using DAP in benzene were measured spectrophotometrically at 320 nm on a Shimadzu QV50 spectrometer thermostatted to 51.0° with a Grant SC 10 circulator.

The temperature of thermostat baths and of the cell compartment was maintained within ±0.2°. Good first-order plots were obtained in all cases for at least 75% reaction, and the error in estimate of k_ψ is ±2%.

Product Analysis.—The initial products formed from neutral and basic aqueous micellar catalysis of (I) and (II) were identified as the corresponding carbamic acids by comparison with known spectra. These were decomposed instantly to the anilines on addition of acid, which were also identified as products in acidic micellar catalysis. At pH >13 a polymer of unknown composition was formed after >6 half-lives. The spectral changes observed for decomposition of (II) by DAP in benzene indicated the formation of 4-nitrophenyl isocyanate.

In contrast to the results of Kurz,[7] this study showed that a decomposition product of NaLS is produced after 6—8 half-lives of the hydrolysis of the phenylurea. This was identified as an alkene but its formation did not interfere with analysis of the rate data.

Apparatus.—N.m.r. spectra were recorded on a Varian

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[1] Part II, C. J. Giffney and C. J. O'Connor, preceding paper.

[2] K. J. Mollett and C. J. O'Connor, unpublished results.

[3] C. J. O'Connor and J. W. Barnett, *J.C.S. Perkin II*, 1973, 1331.

[4] E. F. J. Duynstee and E. Grunwald, *J. Amer. Chem. Soc.*, 1959, **81**, 4540.

[5] P. Mukerjee and K. J. Mysels, *J. Amer. Chem. Soc.*, 1955, **77**, 2937.

[6] A. Kitahara, *Bull. Chem. Soc. Japan*, 1955, **28**, 234.

[7] J. L. Kurz, *J. Phys. Chem.*, 1962, **66**, 2239.

T-60 spectrometer. Spectra of DAP in C_6D_6 were accumulated using a Varian C-1024 time averaging computer and integrating over 128 scans.

Surface tensions were measured on a White Elec. Inst. Co. torsion balance type ' OS ' with a 13 mm platinum ring. A thermostatted cell was maintained at 25° by water circulation from a Grant SC 10 circulator. Values of γ were averaged from five readings. U.v. spectra were recorded on a Unicam SP 800 spectrophotometer. Values of surface tension, γ/N m^{-1}, and rate constants of hydrolysis, k_ψ/s^{-1}, discussed below but not reported are listed in Supplementary Publication No. SUP 21597 (7 pp.).*

RESULTS AND DISCUSSION

Critical Micelle Concentration (*CMC*).—The effect of the addition of small quantities of (I) or (II) in the presence and absence of phosphate buffers on the CMC of A-730 and CTAB has been studied.

TABLE 1

Effect of urea on CMC of surfactants

Surfactant	C/M	CMC(u) ‡ / CMC(o)	Physical method	Ref.
CTAB	0.5	1.04	pH and conductivity	9
	1.0	1.18	pH and conductivity	9
	3.0	1.30	pH and conductivity	9
	6.0	1.62	pH and conductivity	9
NaLS	6.0	2.0	Conductivity	8
Polyoxyethylene (10) nonylphenol	6.0	3.2	Surface tension	10
Polyoxyethylene (30) nonylphenol	6.0	4.0	Surface tension	10

‡ The ratio of CMC in the presence and absence of urea.

Surface Tension Studies.—The surface tension (γ) of A-730 was studied in aqueous solution, with the addition of 8×10^{-6} and 8×10^{-4}M-(I) in water, and with 8×10^{-6}M-(I) and 4×10^{-4}M-(II) in 0.01M-phosphate buffer (pH 6.7). The surface tension of CTAB was studied with the addition of 8×10^{-4}M-(I) and with 4×10^{-4}M-(II) in 0.01M-potassium phosphate buffer (pH 6.7). Measurements were made at 25°.

The values of CMC obtained from plots of log $C_{\text{A-730}}$ or log C_{CTAB} against γ are given in Table 2 together with comparative literature values.

The reference value of A-730 in water is lower than literature values, but is consistent with data interpolated from the manufacturer's specifications.† Addition of trace amounts of (I) causes relatively large increases in CMC, comparable with those which were previously observed only with addition of molar quantities of urea (Table 1) which is well known for its protein denaturing ability. Substitution of a phenyl group onto the urea produces a compound with very large denaturing effects. Addition of 0.01M-potassium phosphate buffer to this system now causes the CMC to fall again, indicating that phosphate acts as a foreign substance increasing the tendency for micellization. Results obtained with (II) in phosphate buffer confirm the tendency of phenylureas to decrease micellization of A-730.

TABLE 2

CMC Values [a] obtained from surface tension and spectral change studies at 25°

Solution	Surface tension 10^5CMC/M	Spectral change 10^5CMC/M
A-730 (reference)	7.07	17.9
A-730–8 × 10^{-4}M-(I)	11.5	27.4
A-730–8 × 10^{-4}M-(I)–buffer [b]		22.0
A-730–8 × 10^{-6}M-(I)	11.5	
A-730–8 × 10^{-6}M-(I)–buffer [b]	8.7	
A-730–4 × 10^{-4}M-(II)–buffer [b]	10.6	
A-730–4 × 10^{-4}M-(II)–buffer [b]		14.2
CTAB–8 × 10^{-4}M-(I)	85.0	
CTAB–4 × 10^{-4}M-(II)–buffer [b]	100.0	

[a] Literature values: A-730, 28 × 10^{-5}M; CTAB, 92 × 10^{-5}M (ref. 11); A-730, 11—13 × 10^{-5}M (ref. 12). [b] 0.01M-Potassium phosphate at pH 6.7.

Addition of (II) on 0.01M-potassium phosphate buffer to CTAB causes the CMC to increase with respect to the literature value. The 7.6% decrease in the CMC with (I) in phosphate buffer is likely to be reversed to a small increase in absence of buffer, in line with the trend observed for (I) in A-730.

Spectral Change Studies.—Gratzer and Beaven [13] found that micelle formation caused a change in the u.v. spectrum of Triton X-100, $H_{17}C_8PhO(CH_2CH_2O)_{10}H$, and we have found similar changes with A-730. Below the CMC the phenolic absorption is indistinct ($\lambda_{\text{max.}}$ 276.0 nm) but above the CMC the absorbance ($\lambda_{\text{max.}}$ 278.0 nm) is well defined and develops a shoulder ($\lambda_{\text{max.}}$ 284.5 nm).

The addition of phenylureas makes large differences to these spectra. These changes are due to charge transfer interactions between the phenyl rings of the ureas and that of A-730.

The values of the CMC obtained from plots of $\lambda_{\text{max.}}$ (nm) against $C_{\text{A-730}}$ for A-730 in water, with the addition of 8×10^{-4}M-(I), and 8×10^{-4}M-(I) in 0.01M-potassium phosphate buffer (pH 6.7), and with the addition of 4×10^{-4}M-(II) are given in Table 2. This last value was obtained by noting the appearance of the shoulder ($\lambda_{\text{max.}}$ 279 nm) as the peak ($\lambda_{\text{max.}}$ 286.0 nm) did not shift. Typical spectral changes at 25° are shown in Figure 1.

Again the CMC is increased by the addition of phenylureas, and phosphate acts as a foreign particle to increase micellization.

El Mendoza *et al.*[14] allow 4% deviation in the value of the CMC from two different experimental methods. Although the values quoted in Table 2 lie outside this

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* For details of Supplementary Publications see *J.C.S. Perkin II*, 1975, Index issue. Items less than 10 pp. are supplied as full-size copies.

† GAF Corporation Technical Bulletin 9670–007.

[8] M. J. Schick, *J. Phys. Chem.*, 1964, **68**, 3585.

[9] W. U. Malik and S. P. Verma, *Kolloid. Z. Polymer*, 1969, **233**, 985.

[10] M. J. Schick and A. H. Gilbert, *J. Colloid Sci.*, 1965, **20**, 464.

[11] P. Mukerjee and K. J. Mysels, ' Critical Micelle Concentrations of Aqueous Sufactant Solutions,' NSRDS–NBS, Washington, 1971.

[12] L. Hsaio, H. N. Dunning, and P. B. Lorenz, *J. Phys. Chem.*, 1956, **60**, 657.

[13] W. B. Gratzer and G. H. Beaven, *J. Phys. Chem.*, 1969, **73**, 2270.

[14] J. El Mendoza, H. C. Gomez, and M. J. Perda, *Grasas y Aceites*, 1973, **24(4)**, 236.

range, they reflect the known dependence of the absolute value of the CMC upon the method used for its determination.

It is realized that the spectral changes we have observed are small, but they are of the same order of magnitude as previous spectral change studies of substrates in micellar environments.[15-17]

Many of the conclusions reached by interpretation of spectral changes appear to be somewhat tenuous [18] and considerable caution is clearly warranted in attributing significance to spectral data, especially for systems for which finite absorption spectral changes and solvent effects therein are incompletely understood. We therefore attribute more reliability to data from surface tension work than to these spectral change determinations of the CMC.

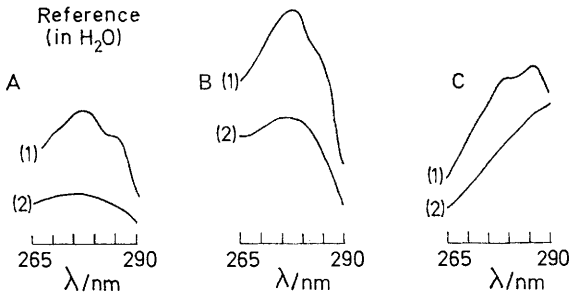

FIGURE 1 Spectra at 25° of A-730 (2) below CMC and (1) above CMC: A, in water; B, in water with added 4-methylphenylurea; and C, added 4-nitrophenylurea

Micellar Effects on Hydrolysis in Aqueous Solution.—All rate measurements were carried out at 101.0°.

Aqueous CTAB ($1—14 \times 10^{-3}$M) (at pH 7) had no effect on the rate of hydrolysis of (I); CTAB ($1—15 \times 10^{-3}$M) in 0.01M-potassium phosphate buffer (pH 6.7) caused small ($\leqslant 1.3$ fold) but irregular rate enhancements of (I) implying involvement of K^+, HPO_4^{2-}, and $H_2PO_4^-$ ions; CTAB (1—18M) in phosphate buffer (pH 6.7) caused the rate profile for (II) to rise to a maximum at C_{CTAB} 3×10^{-3}M (rate enhancement 1.1) and then to fall again.

A-730 ($1—9 \times 10^{-4}$M) in 0.01M-potassium phosphate buffer (pH 6.8) had no effect on hydrolysis of (II) but the profile for (I) was that of a classical sigmoidal curve, followed by a maximum at C_{A-730} 5×10^{-4}M (rate enhancement 1.35) and then a rate decrease. Application of equation (1) [19] [where C_D is the surfactant concentration, k_ψ and k_o are the observed pseudo-first-order rate constant and the rate constant for product formation in the bulk solvent respectively, k_m is the rate constant for product formation in the micellar phase (equal to the maximum in the rate profile at $C_{A-730} >$ CMC), K is the micelle–substrate binding or association constant, and N the aggregation number $= 82$ [11]] to the initial rate increase gave a good straight line from which a value of $K = 12.1 \times 10^5$ l mol^{-1} was obtained. This is higher than binding constants generally found for the reactions with ionic surfactants. The intercept in the plot of equation (1) gave a value of the CMC of 7.48×10^{-5}M and this agrees well with the value obtained from surface tension studies (Table 2).

$$(k_\psi - k_o)/(k_m - k_\psi) = K(C_D - \text{CMC})/N \qquad (1)$$

NaLS ($0—16 \times 10^{-2}$M) in 0.01M-potassium phosphate buffer [pH 6.6 for (I), 6.8 for (II)] causes slight rate enhancement [1.2 for (I), 1.4 for (II)] at *ca.* 4×10^{-2}M-NaLS, and then depression of rate.

Surfactant Effects on the Acid-catalysed Hydrolysis.—In 1M-HCl, the rate of hydrolysis is increased in the presence of both charged and uncharged micelles. But the hydrolysis of (II) is retarded in 1M-HCl. In 0.01M-HCl hydrolysis of both (I) and (II) is inhibited. Results are given in Table 3.

TABLE 3

Micellar effects on rate constants of hydrolysis of 4-methyl- and 4-nitro-phenylurea in acid and base at 101.0°

	$10^5 k_\psi/s^{-1}$			
	Reference	CTAB [a]	A-730 [b]	NaLS [c]
4-Methylphenylurea				
C_{NaOH} 1M	16.0	16.5	19.9	20.6
C_{NaOH} 0.1M	10.5	8.70	9.25	9.30
C_{HCl} 0.96M	13.8	18.0	18.4	18.4
C_{HCl} 0.09M	11.5	9.59	10.5	9.92
4-Nitrophenylurea				
C_{NaOH} 1M	64.8	82.5	79.7	80.6
C_{NaOH} 0.1M	36.7	27.9	19.6	19.5
C_{HCl} 1.11M	9.77	6.38	7.31	7.40
C_{HCl} 0.09M	8.31	5.21	5.18	6.19

[a] C 6×10^{-3}M. [b] C 2×10^{-4}M. [c] C 8×10^{-3}M.

The rate-determining step in the acid-catalysed hydrolysis of phenylureas involves slow cyclic transfer of protons within an already (pre-equilibrium) proton acid substrate *via* a water molecule.[1] It seems that the $NHCONH_2$ group on (II) is in an environment where proton transfer is less easy than in aqueous solution. This result reflects the solubilization of the molecule in the micellar environment.

Surfactant Effects on the Base-catalysed Hydrolysis.—In 1M-NaOH the rates of hydrolysis of (I) and (II) are enhanced but in 0.1M-NaOH the rates are inhibited (Table 3). The large difference in rate between the catalysis observed at 1M-NaOH and the inhibition at 0.1M-NaOH [particularly for (II)] is indicative of a change in mechanism at higher concentrations.

Effect of Temperature on Micellar Catalysis in Aqueous Solution at pH 6.8.—Rate constants of hydrolysis of (I) and (II) were measured at 89.0° and values of activation energies and entropies of activation are given in Table 4. It is realised that these activation parameters are

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[15] S. Riegelman, N. A. Allawala, M. K. Hrenoff, and L. A. Strait, *J. Colloid Sci.*, 1958, **13**, 208.

[16] B. A. Mulley and A. D. Metcalf, *J. Pharm. Pharmacol.*, 1956, **8**, 774.

[17] M. Donbrow and C. T. Rhodes, *J. Chem. Soc.*, 1964, 6166.

[18] J. H. Fendler and L. K. Patterson, *J. Phys. Chem.*, 1971, **75**, 3907.

[19] E. J. Fendler and J. H. Fendler, *Adv. Phys. Org. Chem.*, 1970, **8**, 271.

qualitative only, since they depend on data at only two temperatures. Nevertheless the values of E_a for hydrolysis of (I) are higher than those of (II), and are probably a reflection of the different orientation of the solubilized substrates within the micelles with respect to bulk water.

TABLE 4

Arrhenius parameters for hydrolysis of 4-methyl- (I) and 4-nitro-phenylurea (II) in aqueous micellar solutions

	(I)		(II)	
	E_a/kJ mol^{-1}	ΔS^*/ J K^{-1} mol^{-1}	E_a/kJ mol^{-1}	ΔS^*/ J K^{-1} mol^{-}
CTAB	123	114	84.7	7.66
NaLS	113	84.5	71.0	−26.8
A-730	142	167	64.0	−47.8

Sites of Solubilization.—The addition of (I) and (II) (2 mg, *ca.* 2×10^{-2}M) to 20×10^{-2}M-NaLS (0.5 ml) in D_2O produced little effect on any of the hydrogen atoms in the ^1H n.m.r. spectrum of $H_3C[CH_2]_{10}CH_2SO_4^-$ indicating solubilization at the micellar–water interface only. This is consistent with the very small effect of NaLS on the hydrolysis rate and also with the results of Muller and Johnson [20] who found that urea hardly penetrated the hydrocarbon core of sodium 12,12,13-trifluorododecyl sulphate.

Resemblance of the absorption spectra of the solubilizate in the micellar phase to that in polar solvents is generally interpreted as implying a polar environment of the substrate and *vice versa.* Therefore the resemblance of the u.v. spectra at 25° of (II) in all three micellar solutions to that in H_2O is good evidence for solubilization at the micellar–water interface, or at least in water molecules solubilized in the outer layer of the micelle.[21] The orientation of (II) in CTAB (Figure 2) is probably affected like the 4-nitrophenyl esters of carboxylic acids.[22]

This is in accord with Berezin *et al.*[23] who state that aliphatic molecules or side chains are generally immersed in the hydrophobic core of the micelle. Aromatic molecules or parts thereof are probably (but not always) situated in the hydrophobic core of anionic and nonionic micelles. Molecules with polar substituents are orientated so that the polar groups are in the surface layer and the non-polar portions are immersed in the micellar core. Figure 2 shows the NO_2 group at the micelle water interface held rigidly between the $-\overset{+}{N}(CH_3)_3$ groups. Bimolecular kinetics for (II) are consistent with rate-determining attack by water, solubilized in the micellar environment, on the molecule.

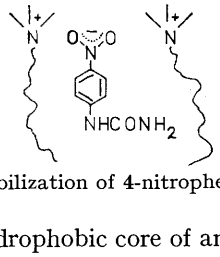

FIGURE 2 Solubilization of 4-nitrophenylurea in CTAB

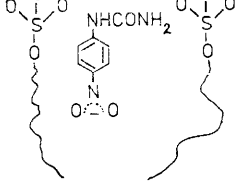

FIGURE 3 Solubilization of 4-nitrophenylurea in NaLS

In NaLS, it is the $NHCONH_2$ group, not NO_2, which will be stabilized at the micelle–water interface (Figure 3). Compound (II) in this orientation would be unable to undergo intramolecular hydrogen shifts in a six-membered transition state,[1] therefore making bimolecular kinetics through rate-determining water attack a more easily accessible route.

The effect of (II) on the phenoxide absorbance of A-730 (Figure 1) indicates a charge transfer interaction, implying deeper penetration of (II) into A-730 than into CTAB or NaLS.

In a micellar solution of A-730, it is probable that the 4-methyl group of (I) is in contact with the hydrocarbon core. This places the two phenyl groups in ideal positions for charge transfer interactions, which are made possible because of resonance structures and the small amount of positive charge resident in the polyoxyethylene chains.[12] The u.v. spectrum indicates that the $NHCONH_2$ group is still in a reasonably polar environment, and proton transfer *via* a water molecule will be possible on a substrate which is hydrogen bonded to the polyoxyethylene groups; similar hydrogen bonding has been found for benzoic acid.[24] A representation of the solubilization of (I) in A-730 is given in Figure 4.

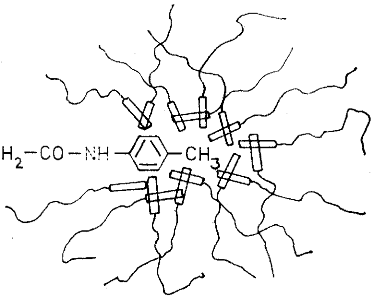

FIGURE 4 Solubilization of 4-methylphenylurea in nonylphenoxypoly(oxyethylene)-14-ethanol (A-730)

In NaLS and CTAB, (I) is expected to be solubilized at or near the micelle water interface.

Studies in Reversed Micelles.—Compound (II) (1.6×10^{-4}M) decomposes at 51° in dry benzene in the presence

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[20] N. Muller and T. W. Johnson, *J. Phys. Chem.*, 1969, **73**, 2042.

[21] N. Muller, in 'Reaction Kinetics in Micelles,' ed. E. H. Cordes, Plenum, New York, 1973.

[22] C. A. Bunton, personal communication.

[23] I. V. Berezin, K. Martinek, and A. K. Yatsimirskii, *Russ. Chem. Rev.*, 1973, 787.

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

of DAP. Lack of substrate solubility prevented measurement of the decomposition rate in pure benzene but this is expected to be negligible. Increasing concentrations of the surfactant increases the decomposition rate. This increase is sigmoidal in the region of the critical micelle concentration and then reaches a plateau (Figure 5). This plateau value was taken as k_m, the rate constant for micellar catalysis. This profile, indicating saturation type kinetics obeying the Michaelis–Menten equation is typical of micellar catalysed reactions.[19,24] Figure 6 indicates that, in addition to micellar catalysis, components of dodecylammonium propionate also enhance the decomposition rate, because at $C_{DAP} > 10 \times 10^{-3}$M the rate continues to increase. Such general acid and general base catalysis by the components is not surprising in view of the general acid and base hydrolysis found in aqueous buffer solutions.[2] A similar effect has also been found for the decomposition of 2,5-dinitrophenyl sulphate in benzene in the presence of alkylammonium carboxylates.[25] The observed rate constant for the decomposition of (II) at a given DAP concentration, k_ψ, can be described by equation (2), where $k_{RNH_3^+}$

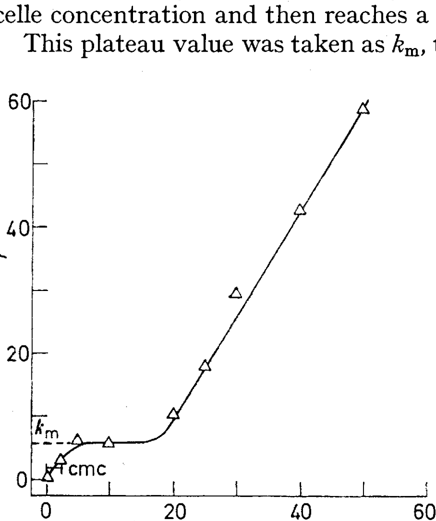

FIGURE 5 Rate constants of hydrolysis of 4-nitrophenylurea as a function of the concentration of dodecylammonium propionate (DAP) in benzene at 51.0°

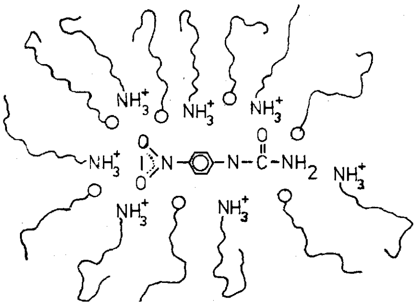

FIGURE 6 Solubilization of 4-nitrophenylurea in DAP

$$k = k_m + (k_{RNH_3^+} + k_{-O_2CR'})(C_{RNH_3^+} + C_{-O_2CR'}) \quad (2)$$

and $k_{-O_2CR'}$ represent rate constants due to dodecylammonium and propionate groups of the surfactant, respectively. Below the CMC, the decomposition is due entirely to $k_{RNH_3^+} + k_{-O_2CR'}$.

The slope of the plot of k_ψ against C_{DAP} (Figure 5) at $C_{DAP} \geqslant 20 \times 10^{-3}$M gives a value of $(k_{RNH_3^+} + k_{-O_2CR'}) = 0.163$ l mol^{-1} s^{-1}.

^{1}H N.m.r. spectroscopy has been utilized for the determination of CMCs and aggregation numbers of alkylammonium carboxylates in chloroform, dichloromethane, benzene, chlorobenzene, carbon tetrachloride, *NN*-dimethylacetamide, and dimethyl sulphoxide.[26] The spectra show quite unequivocally that these detergents exist as $RNH_3^+-O_2CR'$ in these solvents and not as RNH_2-HO_2CR'.

Addition of H_2O (10 µl) to 50×10^{-3}-DAP (10 ml) in dry benzene containing (II) suppressed the decomposition rate at 51° to a negligible amount, presumably to a rate comparable with that in aqueous solution. This decrease is consistent with the proton-donating and -accepting powers inherent in the polar cavity of reversed micelles being greater than the relative abilities of a general acid or a general base to donate or accept protons in aqueous media. Thus proton transfer to a water molecule solubilized in the centre of the reversed micelle competes with the initial pre-equilibrium proton transfer necessary for decomposition.

The rate constant, k_m, for the reversed micellar catalysis of (II) is *ca.* 5.5×10^{-4} s^{-1}. This is *ca.* 3×10^3 times faster than the hydrolysis of (II) in aqueous solution at pH 6.7 (k_ψ *ca.* 1.8×10^{-7} s^{-1}, extrapolated from data at 89—101° [2]). It is not possible to evaluate the rate enhancement with respect to wet benzene but this would certainly be even greater. Previous rate increases for organic reactions in reversed micelles in benzene compared with rates in water have been 210-fold for mutarotation of 2,3,4,6-tetramethyl-α-D-glucose in DAP [27] and 1 880 fold for decomposition of Meisenheimer complexes in dodecylammonium benzoate.[28]

Solubilization in Reversed Micelles.—A qualitative study using a time averaging computer n.m.r. analysis showed that solubilization of kinetic concentrations of (II) in a solution of 0.5M-DAP in C_6D_6 caused a significant shift of the NH_3^+ protons (from δ 8.60 to 6.80) but little difference to chemical shifts of the remaining protons, indicating that the site of solubilization is in the polar cavity of the micelle (Figure 6).

Changes in the CMC as a function of temperature and

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pressure can provide thermodynamic data for micellization;[29,30] however the effects of temperature on the CMC of charged micelles are considerably more complex than those for non-ionic micelles. A knowledge of these and other factors which alter the CMC is desirable and necessary in order to design meaningful kinetic experiments in investigations of micellar catalysis, inhibition, or hydrophobic interactions.

In this investigation we realise that we have used temperatures for the kinetic investigations (101.0 and 89.0° for aqueous detergents and 51.0° for DAP in benzene) which are quite different from those used for surface tension, u.v. spectral, and n.m.r. spectral studies on determination of the CMC and sites of solubilization. Nevertheless the range of detergent concentrations used is far in excess of the small temperature effects on the CMC and will not affect the conclusion that aqueous detergents have little effect on the rate of hydrolysis of phenylureas, whereas DAP in dry benzene causes a marked enhancement of the rate of decomposition of (II).

[5/822 *Received*, *5th May*, 1975]

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