Micellar Effects on the Hydrolysis and Aminolysis of 2,4-Dinitrophenyl Sulphate

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Effects of micellar hexadecyltrimethylammonium bromide (CTAB), sodium dodecyl sulphate (NaLS), polyoxyethylene(20) nonylphenol (Igepal CO-850), 3-(dimethyldodecylammonio)-propane-1-sulphonate (DDAPS) and that of their co-micellar mixtures have been investigated on the nucleophilic reactivity of primary, secondary, and tertiary amines toward 2,4-dinitrophenyl sulphate. Observed second-order rate constants, $k_{2,\mathrm{obs}}$ have been separated into those due to hydrolysis, $k_{2,\mathrm{hyd}}$, and to nucleophilic attack, $k_{2,\mathrm{nuc}}$. Micellar CTAB, DDAPS, and Igepal CO-850 enhance $k_{2,\mathrm{hyd}}$ for the different amines from 4 to 33 fold, while micellar NaLS has no appreciable effect. A more dramatic result is the complete suppression of $k_{2,\mathrm{nuc}}$ by micellar CTAB, DDAPS, and mixtures of CTAB and Igepal CO-850 for reactions of hydrazine and morpholine. Sensitivities of hydrolysis to amine basicity (Brønsted β-values) are greater in micellar CTAB, DDAPS, and Igepal CO-850 than in pure water.

ASSOCIATION colloids, or micelles, affect the rates of numerous reactions.[1,2] Rate enhancement or retardation is the consequence of substrate solubilization and differential reaction rates in the micellar and bulk aqueous phases.

Under favourable conditions it is expected that micelles can alter the product distribution of complex reactions. Although this type of application of micelles is of obvious importance, no mechanistic study has been directed toward elucidation of the factors involved.

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Since the nucleophilic reactions of amines with nitrophenyl sulphate[3] and phosphate[4] esters have been investigated and since we have reported a modest micellar catalysis of the hydrolysis of 2,4-dinitrophenyl sulphate,[5] we chose the reaction of amines with the latter ester as the subject of our investigation. The reaction of amines with 2,4-dinitrophenyl sulphate can, of course, result in the formation of 2,4-dinitrophenol and *N*-substituted 2,4-dinitroanilines. We have examined in detail the effects of charged and neutral micelles on the rate of this reaction and report that in several cases association colloids completely suppress the formation of the anilines.

EXPERIMENTAL AND RESULTS

Preparation and purification of 2,4-dinitrophenyl sulphate has been described.[6] A spectrophotometric assay of 2,4-dinitrophenoxide ion released on complete hydrolysis indicated that 88—93% of the initial salt was present as the active sulphate, the impurity being the hydrolysis products.

Reagent grade 2-picoline (Aldrich), 4-picoline (Aldrich), morpholine (Fisher), pyridine, and piperidine (J. T. Baker) were redistilled before use. Reagent grade nicotinamide (Fisher), imidazole (Aldrich), hydrazine (Fisher), glycine (J. T. Baker), and n-butylamine (Fisher) were checked for purity (m.p. or b.p. and spectra) and were used without further purification.

Doubly distilled deionized water was used for the preparation of the buffer and surfactant solutions. Since electrolytes are known to affect micellar parameters,[2] the buffer concentration was kept relatively low for each amine and no salt was added to maintain constant electrolyte strength. The pH of the solutions was adjusted by addition of standard 1·00 or 0·10M-HCl or -NaOH (B.D.H.) and was measured with a Radiometer PHM-26 expanded-scale pH-meter.

The surfactants, hexadecyltrimethylammonium bromide, CTAB (Eastman, practical grade) and sodium dodecyl sulphate, NaLS (City Chemical Corp.) were purified by established methods.[2,5] Polyoxyethylene (20) nonylphenol (Igepal CO-850) and polyoxyethylene (24) dinonylphenol (Igepal DM-730) from General Aniline and Film Corporation were used without further purification. The preparation of 3-(dimethyldodecylammonio)propane-1-sulphonate (DDAPS) has been described.[7] Decylammonium bromide (DAB) was prepared by reaction of n-decylamine (Aldrich) with a *ca.* 0·25 mole per mole excess of ammonium bromide in hot methanol solution.[8] After three recrystallizations from acetone and drying *in vacuo*, the white crystals of DAB decomposed at 195—197 °C. Hexadecylpyridinium chloride, HDPC (City Chemical Corp., practical grade) was purified by at least two recrystallizations from ethanol–ether (1 : 1 v/v) and after thorough drying *in vacuo* over P_2O_5 decomposed at *ca.* 175 °C.

Surface tension–detergent concentration profiles were obtained at 25·0 °C for each detergent by use of a Cenco du Noüy tensiometer with a 6 cm platinum–iridium ring. The surface tension was calculated from an expression[9] involving the measured force, ring dimensions, and the correction factor. The absence of minima[10] in plots of the surface tension against concentration and the good agreement of the critical micelle concentration values, obtained from these plots, with those in the literature[11] indicate the absence of impurities in the surfactants.

The pK_a values for nicotinamide,[12] pyridine,[13] 2-picoline,[13] 4-picoline,[13] imidazole,[14] hydrazine,[15] morpholine,[15] glycine,[16] n-butylamine,[15] and piperidine[15] were obtained from the literature. The pK_a values for pyridine in $4·60 \times 10^{-3}$M-CTAB, morpholine in $4·60 \times 10^{-3}$M-CTAB, and pyridine in $4·05 \times 10^{-2}$M-NaLS were determined by plotting optical absorbance as a function of pH. The pK_a values determined in the presence of detergents agreed with literature values in pure water.

The rate of formation of products was monitored at 360 nm. Reactions were initiated by the addition of *ca.* 30 μl of 5×10^{-3}M-2,4-dinitrophenyl sulphate in acetonitrile–water (3 : 1 v/v) to 2·5 ml of the reaction solution which was pre-equilibrated at 39·0 °C in the thermostatted cell compartment of a Beckman Kintrac VII spectrophotometer. The overall concentration of 2,4-dinitrophenyl sulphate in the mixture was $1—6 \times 10^{-5}$M. The volume of acetonitrile injected into the reaction solution with the substrate is <1% of the total volume present in the solution and has a negligible effect on the rate constants.[6] The temperature was monitored inside the cells and was maintained within 0·05 °C. The pH of each solution was determined before and after each run and those with a change in pH greater than ±0·05 were discarded. The rates of reaction were followed to over 90% completion and excellent pseudo-first-order plots were obtained. Pseudo-first-order rate constants, $k_{1.\text{obs}}$, were calculated by means of a computer with a least-squares programme.[17]

Pseudo-first-order rate constants plotted against free amine concentration gave good straight lines (Figure 1). Free amine concentrations were calculated from the pH of the solution and the pK_a values of the amines. The second-order rate constants, $k_{2.\text{obs}}$ also were calculated from the data by use of the least-squares programme. The intercepts obtained from the $k_{2.\text{obs}}$ values and the concentration of the free amine by use of the programme agreed

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well with those determined in the absence of the amine. Two aromatic products are possible from the reaction of 2,4-dinitrophenyl sulphate with a primary or secondary amine, namely 2,4-dinitrophenolate ion and an *N*-substituted 2,4-dinitroaniline. Both absorb strongly at 360 nm; however, at pH 2 the phenoxide ion is protonated and therefore nearly colourless.

The rates of hydrolysis and of nucleophilic attack at the aromatic carbon were determined by acidifying the mixture on completion of the reaction and measuring the absorbance due mainly to the substituted aniline. The overall second-order rate constant was separated into rate constants due to hydrolysis ($k_{2.\mathrm{hyd}}$) and to nucleophilic attack ($k_{2.\mathrm{nuc}}$) by use of equations (1) and (2), where [P] is the concentration of the phenoxide ion and [An] is the concentration of the substituted aniline. These concentrations were determined from the extinction coefficients and absorbances by use of equations (3) and (4) where $A_{0(\mathrm{b})}$, $A_{0(\mathrm{a})}$, $A_{\infty(\mathrm{b})}$, and $A_{\infty(\mathrm{a})}$ are the initial and final absorbances in basic and acidic solution, respectively; $\varepsilon_{\mathrm{p(b)}}$ and $\varepsilon_{\mathrm{p(a)}}$ are the experimentally determined molar extinction coefficients of the phenoxide ion ($\varepsilon_{360\,\mathrm{nm}} = 1{\cdot}36 \times 10^4$ l mol^{-1} cm^{-1}) and the phenol ($\varepsilon_{360\,\mathrm{nm}} = 2{\cdot}40 \times 10^3$ l mol^{-1} cm^{-1}), respectively, and $\varepsilon_{\mathrm{An(b)}}$ and $\varepsilon_{\mathrm{An(a)}}$ are those for the substituted anilines in basic and acidic solution. The solution of equations (3) and (4) for the two unknown concentrations was carried out on a computer with a determinant algorithm.

$$k_{2.\mathrm{obs}} = k_{2.\mathrm{hyd}} + k_{2.\mathrm{nuc}} \tag{1}$$

$$k_{2.\mathrm{hyd}} = k_{2.\mathrm{obs}}\left(\frac{[\mathrm{P}]}{[\mathrm{P}] + [\mathrm{An}]}\right) \tag{2}$$

$$A_{\infty(\mathrm{b})} = A_{0(\mathrm{b})} + \varepsilon_{\mathrm{p(b)}}[\mathrm{P}] + \varepsilon_{\mathrm{An(b)}}[\mathrm{An}] \tag{3}$$

$$A_{\infty(\mathrm{a})} = A_{0(\mathrm{a})} + \varepsilon_{\mathrm{p(a)}}[\mathrm{P}] + \varepsilon_{\mathrm{An(a)}}[\mathrm{An}] \tag{4}$$

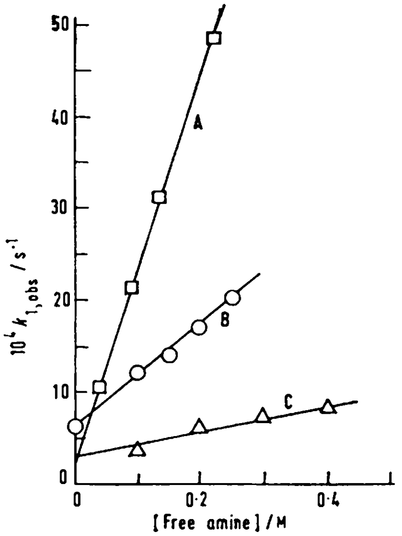

FIGURE 1 Plot of the pseudo-first-order rate constants, $k_{1.\mathrm{obs}}$, against the free amine concentration for A. morpholine in NaLS; B. nicotinamide in CTAB and Igepal CO-850; and C. 2-picoline in Igepal CO-850

The extinction coefficients of the *N*-substituted anilines were determined by measuring the absorbance of known concentrations at the appropriate pH. The *N*-morpholino- and piperidino-anilines were prepared by a method described by Vogel [18] in which 1-chloro-2,4-dinitrobenzene is refluxed with the amine. *N*-2,4-Dinitrophenylmorpholine (m.p. 118—119 °C; lit.,[19] 118 °C) gave extinction coefficients of $1{\cdot}07 \times 10^4$ and $1{\cdot}06 \times 10^4$ l mol^{-1} cm^{-1} at 360 nm in pH 10 and 2 aqueous solutions, respectively. *N*-2,4-Dinitrophenylpiperidine (m.p. 90—91 °C; lit.,[20] 91—93 °C) has extinction coefficients of $9{\cdot}30 \times 10^3$ and $7{\cdot}80 \times 10^3$ l mol^{-1} cm^{-1} at 360 nm in pH 8 and 2 aqueous solutions, respectively. *N*-2,4-Dinitrophenylhydrazine (Matheson Coleman and Bell) yielded extinction coefficients of $1{\cdot}11 \times 10^4$ and $7{\cdot}50 \times 10^3$ l mol^{-1} cm^{-1} at 360 nm in pH and 8 and 2 aqueous solutions, respectively. *N*-2,4-Dinitrophenylimidazole (m.p. 144 °C; lit.,[19] 144 °C) was prepared by a method of Zahn and Pfannmüller,[21] and yielded extinction coefficients of $6{\cdot}96 \times 10^3$ and $2{\cdot}05 \times 10^2$ l mol^{-1} cm^{-1} at 360 nm in pH 10 and 2 aqueous solutions, respectively.

Rate constants for the neutral hydrolysis of 2,4-dinitrophenyl sulphate in the presence of micellar surfactants at 39·0 °C are in Table 1. The value for the hydrolysis of 2,4-dinitrophenyl sulphate in $4{\cdot}60 \times 10^{-3}$M-CTAB obtained at 39·0 °C agreed well with the value predicted from the Arrhenius parameters [5] determined for the hydrolysis in $6{\cdot}00 \times 10^{-3}$M-CTAB.

The second-order rate constants as well as values for $k_{2.\mathrm{hyd}}$ and $k_{2.\mathrm{nuc}}$ for the reactions of ten amines with 2,4-dinitrophenyl sulphate, in aqueous solution at 39·0 °C, in the absence of surfactants are given in Table 2.

Tables 3—8 summarize values of $k_{2.\mathrm{obs}}$, $k_{2.\mathrm{hyd}}$, and $k_{2.\mathrm{nuc}}$ for the same reaction in the presence of micellar CTAB, DDAPS, CTAB + Igepal CO-850, DDAPS + Igepal CO-850, Igepal CO-850, and NaLS, respectively.

TABLE 1

Pseudo-first-order rate constants for the hydrolysis of 2,4-dinitrophenyl sulphate in micellar solutions [a]

Surfactant	CMC/M	Concn./M	$10^4 k_{1.\mathrm{hyd}}$/ s^{-1}
None			1·45
None			0·27 [b]
NaLS	$8{\cdot}1 \times 10^{-3}$	$4{\cdot}05 \times 10^{-2}$	1·33
CTAB	$7{\cdot}8 \times 10^{-4}$	$4{\cdot}60 \times 10^{-3}$	3·83
Igepal DM-730		$1{\cdot}00 \times 10^{-2}$	0·68 [b]
Igepal CO-580	$1{\cdot}5 \times 10^{-4}$	$7{\cdot}50 \times 10^{-4}$	1·48
CTAB + Igepal CO-850	$7{\cdot}8 \times 10^{-4}$ $1{\cdot}5 \times 10^{-4}$	$4{\cdot}60 \times 10^{-3}$ $7{\cdot}50 \times 10^{-4}$	4·83
DDAPS	$1{\cdot}2 \times 10^{-3}$	$5{\cdot}00 \times 10^{-2}$	5·10
HDPC [c]	$9{\cdot}0 \times 10^{-4}$	$4{\cdot}50 \times 10^{-3}$	5·22
DAB [d]	$1{\cdot}6 \times 10^{-2}$	$8{\cdot}00 \times 10^{-2}$	9·20

[a] In the presence of $2{\cdot}5 \times 10^{-3}$M-$Na_2B_4O_7$ buffer at 39·00 °C and pH 8·20, unless specified otherwise. [b] At 25·00 °C: data from ref. 5. [c] Hexadecylpyridinium chloride. [d] Decylammonium bromide at pH 6·95.

The correlation coefficient is a measure of the linear association between random variables and an *r* value of

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Table 2

Second-order rate constants for nucleophilic reactions with 2,4-dinitrophenyl sulphate in the absence of surfactants [a]

Nucleophile	pK_a [b]	[Free amine]/M	$10^4k_{2.\mathrm{obs}}$/l mol^{-1} s^{-1}	Corrn. coefft.	$10^2k_{2.\mathrm{hyd}}$/l mol^{-1} s^{-1}	$10^4k_{2.\mathrm{nuc}}$/l mol^{-1} s^{-1}
Nicotinamide	3·40	0·1—0·25	4·67	0·9999	4·67	
Pyridine	5·17	0·025—0·5	7·45	0·9929	7·45	
2-Picoline	5·97	0·2—0·5	2·98	0·9908	2·98	
4-Picoline	6·02	0·2—0·6	18·9	1·0000	18·9	
Imidazole	6·95	0·2—0·5	1·68	0·9987	1·68	*e*
Hydrazine	8·10	0·07—0·3	188	0·9968	52·3	136
Morpholine	8·36	0·045—0·23	208	0·9995	17·5	191
Glycine	9·6	0·01—0·37	39·5	0·9997	*f*	*f*
n-Butylamine	10·59	0·02—0·21 [d]	97·8	0·9882	*f*	*f*
Piperidine	11·22	0·01—0·036 [d]	3680	0·9780	73·7	3610

[a] In the presence of 2·5 × 10^{-3}M-$Na_2B_4O_7$ buffer at 39·00 °C, unless specified otherwise. [b] See Experimental and Results sections for references. [c] Calculated from equations (3) and (4). [d] In 2·0 × 10^{-2}M-$NaHCO_3$ buffer. [e] C–O bond cleavage <1%, not detectable by absorbance difference on acidification. [f] Not determined.

Table 3

Second-order rate constants for nucleophilic reactions with 2,4-dinitrophenyl sulphate in the presence of 4·6 × 10^{-3}M-CTAB [a]

Nucleophile	pK_a [b]	[Free amine]/M	$10^2k_{2.\mathrm{obs}}$/l mol^{-1} s^{-1}	Corrn. coefft.	$10^2k_{2.\mathrm{hyd}}$/l mol^{-1} s^{-1}	$10^2k_{2.\mathrm{nuc}}$/l mol^{-1} s^{-1}
Nicotinamide	3·40	0·1—0·25	0·435	0·9618	0·435	
Pyridine	5·17	0·075—0·25	2·48	0·9706	2·48	
2-Picoline	5·97	0·1—0·4	0·55	0·9948	0·55	
4-Picoline	6·02	0·1—0·4	3·03	0·9974	3·03	
Imidazole	6·95	0·2—0·5 [d]	0·30	0·9983	0·30	*e*
Hydrazine	8·10	0·055—0·32	0·385	1·0000	0·385	*e*
Morpholine	8·36	0·047—0·24	1·08	0·9996	1·08	*e*
Glycine	9·6	0·214—0·350	0·28	0·9996	*f*	*f*
n-Butylamine	10·59	0·04—0·09 [d]	1·41	0·9981	*f*	*f*
Piperidine	11·22	0·01—0·07 [d]	17·6	0·9756	9·83	7·72

See Table 2 for notes *a*—*f*.

Table 4

Second-order rate constants for nucleophilic reactions with 2,4-dinitrophenyl sulphate in the presence of 5·0 × 10^{-2}M-DDAPS [a]

Nucleophile	pK_a [b]	[Free amine]/M	$10^2k_{2.\mathrm{ob}^{\mathrm{s}}}$/l mol^{-1} s^{-1}	Corrn. coefft.	$10^2k_{2.\mathrm{hyd}}$/l mol^{-1} s^{-1}	$10^2k_{2.\mathrm{nuc}}$ [c]/l mol^{-1} s^{-1}
Nicotinamide	3·40	0·1—0·25	0·467	0·9997	0·467	
Pyridine	5·17	0·075—0·30	2·12	0·9695	2·12	
2-Picoline	5·97	0·1—0·4	0·422	0·9998	0·422	
4-Picoline	6·02	0·1—0·4	2·32	0·9821	2·32	
Imidazole	6·95	0·2—0·5 [d]	0·268	0·9821	0·268	*e*
Hydrazine	8·10	0·06—0·31	0·445	0·9920	0·455	*e*
Morpholine	8·36	0·06—0·24	0·968	0·9994	0·968	*e*
Glycine	9·6	0·119—0·306	0·189	0·9968	*f*	*f*
Piperidine	11·22	0·01—0·034 [d]	14·9	0·9997	6·99	7·88

See Table 2 for notes *a*—*f*.

Table 5

Second-order rate constants for nucleophilic reactions with 2,4-dinitrophenyl sulphate in the presence of 4·6 × 10^{-3}M-CTAB and 4·6 × 10^{-3}M-Igepal CO-850 [a]

Nucleophile	pK_a [b]	[Free amine]/M	$10^2k_{2.\mathrm{abs}}$/l mol^{-1} s^{-1}	Corrn. coefft.	$10^2k_{2.\mathrm{hyd}}$/l mol^{-1} s^{-1}	$10^2k_{2.\mathrm{nuc}}$ [c]/l mol^{-1} s^{-1}
Nicotinamide	3·40	0·1—0·25	0·583	0·9978	0·583	
2-Picoline	5·97	0·1—0·4	0·508	0·9896	0·508	
4-Picoline	6·02	0·1—0·3	3·72	1·0000	3·72	
Imidazole	6·95	0·2—0·5 [d]	0·36	0·9942	0·36	*e*
Hydrazine	8·10	0·06—0·21	0·662	0·9788	0·662	*e*
Morpholine	8·36	0·046—0·24	0·835	0·9883	0·835	*e*
Piperidine	11·22	0·01—0·031 [d]	15·62	0·9972	7·42	8·20

See Table 2 for notes *a*—*f*.

TABLE 6

Second-order rate constants for nucleophilic reactions with 2,4-dinitrophenyl sulphate in the presence of $4·6 \times 10^{-3}$M-DDAPS and $4·6 \times 10^{-3}$M-Igepal CO-850 [a]

Nucleophile	pK_a [b]	[Free amine] M	$10^4k_{2.\text{obs}}$ l mol^{-1} s^{-1}	Corrn. coefft.	$10^4k_{2.\text{hyd}}$ l mol^{-1} s^{-1}	$10^4k_{2.\text{nuc}}$ [c] l mol^{-1} s^{-1}
Pyridine	5·17	0·075—0·15	112·8	0·9891	113	
Imidazole	6·95	0·2—0·5 [d]	8·08	0·9854	8·08	*e*
Glycine	9·6	0·088—0·288	7·37	0·9698	*f*	*f*
Piperidine	11·22	0·01—0·03 [d]	1880	0·9906	352	1530

See Table 2 for notes *a*—*f*.

TABLE 7

Second-order rate constants for nucleophilic reactions with 2,4-dinitrophenyl sulphate in the presence of $4·6 \times 10^{-3}$M-Igepal CO-850 [a]

Nucleophile	pK_a	[Free amine] M	$10^4k_{2.\text{obs}}$ l mol^{-1} s^{-1}	Corrn. coefft.	$10^4k_{2.\text{hyd}}$ l mol^{-1} s^{-1}	$10^4k_{2.\text{nuc}}$ [c] l mol^{-1} s^{-1}
Nicotinamide	3·40	0·1—0·25	7·67	0·9754	7·67	
Pyridine	5·17	0·075—0·25	19·3	0·9947	19·3	
2-Picoline	5·97	0·1—0·40	16·6	0·9845	16·6	
4-Picoline	6·02	0·2—0·5	74·0	0·9725	74·0	
Imidazole	6·95	0·2—0·5 [d]	4·75	0·9926	4·75	*e*
Hydrazine	8·10	0·07—0·29	144	0·9937	37·8	106
Morpholine	8·36	0·045—0·23	217·8	0·9960	56·5	161
Glycine	9·6	0·096—0·27	24·9	0·9963	*f*	*f*
Piperidine	11·22	0·01—0·04 [d]	2720	0·9885	117·2	2610

See Table 2 for notes *a*—*f*.

TABLE 8

Second-order rate constants for nucleophilic reactions with 2,4-dinitrophenyl sulphate in the presence of $4·05 \times 10^{-2}$M-NaLS [a]

Nucleophile	pK_a [b]	[Free amine] M	$10^4k_{2.\text{obs}}$ l mol^{-1} s^{-1}	Corrn. coefft.	$10^4k_{2.\text{hyd}}$ l mol^{-1} s^{-1}	$10^4k_{2\ \text{nuc}}$ [c] l mol^{-1} s^{-1}
Nicotinamide	3·40	0·1—0·25	7·33	0·9983	7·33	
Pyridine	5·17	0·1—0·30	9·77	0·9706	9·77	
2-Picoline	5·97	0·2—0·5	5·57	0·9899	5·57	
4-Picoline	6·02	0·2—0·6	40·3	0·9785	40·3	
Imidazole	6·95	0·2—0·5 [d]	14·2	0·9895	14·2	*e*
Hydrazine	8·10	0·065—0·28	217	0·9992	80·8	136
Morpholine	8·36	0·04—0·22	211·0	0·9992	42·0	169·0
Glycine	9·6	0·048—0·153	46·8	0·9974	*f*	*f*
Piperidine	11·22	0·015—0·048 [d]	2260	0·9949	167·8	2190

See Table 2 for notes *a*—*f*.

TABLE 9

Micellar effects on $k_{2.\text{obs}}$ for the reaction of amines with 2,4-dinitrophenyl sulphate at 39·00 °C

	$k_{2.\text{obs}}{}^{\text{m}}/k_{2.\text{obs}}{}^{\text{H}_2\text{O}}$					
Amine	$4·6 \times 10^{-3}$M-CTAB	$5·0 \times 10^{-2}$M-DDAPS	$4·6 \times 10^{-3}$M-CTAB + $4·6 \times 10^{-3}$M-Igepal CO-850	$4·6 \times 10^{-3}$M-DDAPS + $4·6 \times 10^{-3}$M-Igepal CO-850	$4·6 \times 10^{-3}$M-Igepal CO-850	$4·05 \times 10^{-2}$M-NaLS
Nicotinamide	9·31	10·0	12·5		1·64	1·57
Pyridine	33·3	28·5		15·1	2·59	1·31
2-Picoline	18·5	14·2	17·0		5·57	1·87
4-Picoline	16·1	12·3	19·7		3·92	2·14
Imidazole	17·9	16·0	21·4	4·81	2·82	8·45
Hydrazine	0·23	0·24	0·35		0·76	1·15
Morpholine	0·52	0·47	0·40		1·05	1·01
Glycine	0·72	0·48		0·20	0·63	1·2
n-Butylamine	1·44					
Piperidine	0·47	0·40	0·42	0·51	0·74	0·61

0·99 would signify that 100 r^2 or 98% of the variation in y is explained by differences in x.[17] The second-order rate constants generally had correlation coefficients greater than 0·99 and all data with a correlation coefficient less than 0·96 were discarded. Since such correlations for second-order rate constants had been obtained from 4—6 data points (Figure 2), good correlation coefficients are more significant than those obtained for the Brønsted slopes (Table 10) containing 3 points. Nevertheless even in this case internal consistency is indicated by the correlation coefficients. No correlation coefficient is given for data obtained from less than three points.

TABLE 10

Brønsted slopes for $k_{2.\text{hyd}}$ in water and in the presence of micellar surfactants [a]

	Brønsted slopes (β)		
Surfactants	Tertiary amines	Correlation coefft.	Secondary [b] amines
None	0·21	0·925	0·22
CTAB	0·34	0·974	0·34
DDAPS	0·28	0·963	0·30
CTAB and Igepal	0·31		0·33
Igepal CO-850	0·35	0·953	0·11
NaLS	0·25	0·844	0·21

[a] See Tables 2—8 for concentrations and experimental conditions. [b] Slopes are based on two points.

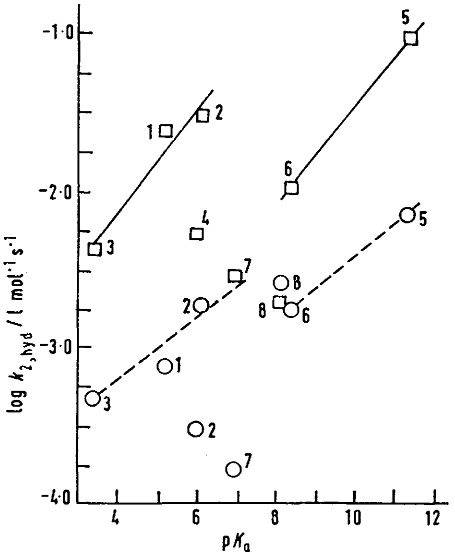
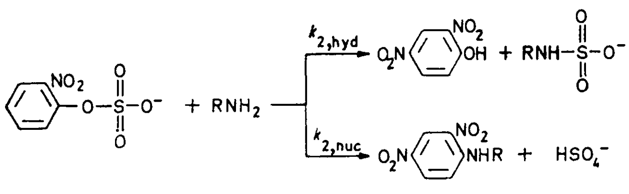


FIGURE 2 Brønsted plots of log $k_{2.\text{hyd}}$ against pK_a of the amine for reactions of 2,4-dinitrophenyl sulphate in CTAB (□, ——) and in water (○, — —). Rate constants for hydrazine are statistically corrected. Points are as follows: 1, pyridine; 2,4-picoline; 3, nicotinamide; 4,2-picoline; 5, piperidine; 6, morpholine; 7, imidazole; 8, hydrazine

DISCUSSION

Neutral Hydrolysis.—Cationic micellar surfactants enhance the rate of neutral hydrolysis of 2,4-dinitrophenyl sulphate at 39·0 °C (Table 1) substantiating previous results at other temperatures.[5] It is noteworthy that the feeble catalysis by micellar non-ionic surfactants is specific: Igepal DM-730 enhances the rate by a factor of 2·6 while Igepal CO-850 has no effect on it. It is more significant, however, that a mixture of CTAB and Igepal CO-850 is a better catalyst than CTAB alone probably by virtue of the lower charge density of the co-micelle. A similar situation has been encountered in the micellar-catalysed decarboxylation of 6-nitrobenzisoxazole-3-carboxylate ion.[22]

Aminolysis.—Reactions of amines with 2,4-dinitrophenyl sulphate can result in the formation of phenoxide ions and a sulphate or sulphate ion, *via* S–O bond fission, or alternatively, in the case of primary and secondary amines, in the production of *N*-substituted anilines and sulphate or hydrogen sulphate ions *via* C–O bond cleavage (see Scheme). The general behaviour in water is quite similar to that observed for the nucleophilic reactions of amines with *p*-nitrophenyl sulphate.[3] The order of rate enhancement for $k_{2.\text{hyd}}$ by the amines is generally tertiary > secondary > primary; hydrazine exhibits the 'α-effect';[23] there is a tendency for the reactivities of secondary and tertiary amines to fall into distinct groups; and the reaction rates are insensitive to the basicity of the nucleophile (Table 2). The observed β-value of 0·21 (Figure 2) compares well with corresponding values of 0·20, 0·22, and 0·13 determined for reactions of amines with *p*-nitrophenyl sulphate,[3] with phosphoramidate,[24] and with *p*-nitrophenyl phosphate dianion,[4] respectively. The implications of these results are, of course, that little bond formation has been achieved between the incoming nucleophile and 2,4-dinitrophenyl sulphate in the transition state.



SCHEME

No kinetic or spectrophotometric evidence has been added for the accumulation of a σ-, or Meisenheimer-type, complex in the nucleophilic attack of amines on the activated aromatic carbon atom of 2,4-dinitrophenyl sulphate. While formation of this type of intermediate in the reaction of *p*-nitrophenyl phosphate with piperidine[25] and in other systems[26] has been demon-

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strated, it appears that even in the case of dinitro-substituted phenyl sulphates the rate-determining step remains the addition of the nucleophile rather than the expulsion of the leaving group.

Cationic micellar CTAB, zwitterionic DDAPS, and non-ionic Igepal CO-850 enhance the overall reactivity, $k_{2,\text{obs}}$, of nicotinamide, pyridine, 2- and 4-picoline, and imidazole with 2,4-dinitrophenyl sulphate appreciably while micellar NaLS, with the exception of imidazole, has no significant effect on the rate (Table 9). The observed second-order rate constants for these amines are due exclusively to hydrolysis. For nicotinamide, 2- and 4-picoline, and imidazole the catalysis by co-micellar CTAB and Igepal CO-850 is greater than by CTAB alone. A similar, although less pronounced, situation prevails in mixed co-micellar DDAPS and Igepal CO-850. Lack of sufficient data for the micellar parameters in these systems does not warrant a meaningful mechanistic discussion of factors involved therein at the present time.

Reactions of hydrazine, morpholine, and piperidine with 2,4-dinitrophenyl sulphate in water results in predominant nucleophilic attack at the aromatic carbon atom (Table 2). The fraction of C–O bond cleavage in water for the overall reaction in the presence of these amines increased from 0·73 for hydrazine to 0·92 and 0·98 for the secondary amines, morpholine, and piperidine, respectively. No C–O bond cleavage was observed in the reaction with imidazole. The type of bond cleavage was not experimentally determined for glycine and n-butylamine. Although the overall second-order rate constants are decreased by all micellar surfactants (Table 9), $k_{2,\text{hyd}}$ for morpholine and piperidine are enhanced by factors of 6·2 and 13·3 by CTAB, by factors of 5·5 and 4·5 by DDAPS, and by factors of 3·2 and 1·6 by Igepal CO-850. A more dramatic result is the complete suppression of aniline formation by hydrazine and morpholine in the presence of micellar CTAB, DDAPS, and mixtures of CTAB and Igepal. In the case of piperidine $k_{2,\text{nuc}}{}^{\text{H}_2\text{O}}/k_{2,\text{nuc}}{}^{\text{CTAB}} = 4{\cdot}7$. NaLS, not unexpectedly, has little effect on the rate of nucleophilic attack. These results clearly indicate that the relative extent of competing reactions can be altered profoundly by micellar surfactants and, indeed, to the point of complete suppression of one or more reactions in some cases. The synthetic utility and industrial potential are self-evident.

The validity of the established mechanism for micellar catalysis [2] has been confirmed for the pyridine-catalysed hydrolysis of 2,4-dinitrophenyl sulphate at different CTAB concentrations. The usual saturation-type kinetics have been observed. A good linear relationship (Figure 3), with a correlation coefficient of 0·9892, has been observed on plotting the left-hand side of equation (5) against C_D * where $k_{2,\text{obs}}{}^{\text{CTAB}}$, $k_{2,\text{obs}}{}^{\text{H}_2\text{O}}$, and $k_{2,\text{obs}}{}^{\text{m}}$ are the observed second-order rate constants at a given CTAB concentration, in water, and in the micellar CTAB phase; C_D is the stoicheiometric surfactant concentration and CMC is the critical micelle concentration. Assuming the aggregation number, N, to be 61,[2] we calculate the binding constant K to be $7{\cdot}7 \times 10^5$ l mol^{-1}. The intercept of the calculated linear equation gave a critical micelle concentration of $5{\cdot}9 \times 10^{-4}$M. This kinetically determined critical micelle concentration is somewhat lower than the critical micelle concentration obtained by surface tension measurements, but can reasonably be attributed to 2,4-dinitrophenyl sulphate- and pyridine-induced micellization of the surfactant and hence a decrease in the critical micelle concentration.[2] A binding constant of $1{\cdot}9 \times 10^5$ l mol^{-1} was obtained previously from an analogous treatment of the CTAB-catalysed neutral hydrolysis of 2,4-dinitrophenyl sulphate.[5]

$$\frac{k_{2,\text{obs}}{}^{\text{CTAB}} - k_{2,\text{obs}}{}^{\text{H}_2\text{O}}}{k_{2,\text{obs}}{}^{\text{m}} - k_{2,\text{obs}}{}^{\text{CTAB}}} = \frac{K}{N}\,(C_\text{D} - \text{CMC}) \qquad (5)$$

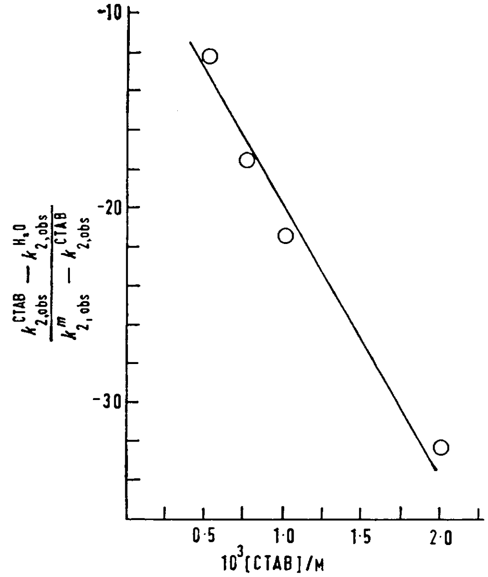

FIGURE 3 Binding constant, K, plot according to equation (5) for the reaction of pyridine with 2,4-dinitrophenyl sulphate in CTAB at 39·00 °C.

It is interesting to compare the sensitivities of the hydrolysis to amine basicity in water with those in micellar surfactants (Figure 2 and Table 10). The Brønsted β-value is greater in cationic CTAB, non-ionic Igepal CO-850, and zwitterionic DDAPS than in water. These results are explicable in terms of greater bond formation in the transition state in micellar solutions than in water. Micellar catalysis is, at least in part, the consequence of a shift of the transition state toward products as compared with that in water. This postulate agrees well with our previous n.m.r. observation that the *in situ* hydrolysis product of 2,4-dinitrophenyl sulphate lies in a more polar environment in micellar

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* Consult ref. 2 for the assumptions made in the derivation of this equation.

DDAPS than its parent molecule.[7] Lack of a more pronounced catalysis for the neutral hydrolysis may well be the consequence, in part, of an energy loss in transferring the initial state of the substrate to a more polar environment in the transition state. The effects of micelles on the amine-catalysed hydrolysis and on the nucleophilic attack by them may be primarily due to changes in the micro-environment of both the substrates and of the transition states by a contribution of electrostatic and hydrophobic interactions.

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