MICELLAR CATALYSIS OF ORGANIC REACTIONS. 28.* A COMPARISON OF THE CATALYTIC EFFECTS OF MICELLES CONTAINING BROMIDE AND FLUORIDE COUNTERIONS ON SOME S_NAr AND $B_{Ac}2$ REACTIONS

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The catalytic effects of micelles of cetyltrimethylammonium bromide (CTAB) and fluoride (CTAF) on several S_NAr and $B_{Ac}2$ reactions were studied. Rate versus detergent concentration curves predicted by the pseudophase models PPIE (ion exchange) for CTAB studies and PPMA (mass action) for the CTAF studies were fitted to the experimental results to determine the best values of the substrate binding constant (K_s), the second-order rate constant for reaction in the micelle (k_2^M) and the exchange constant $K^{OH/X}$ (PPIE) or binding constant (PPMA) for the counterions. Better catalysis by micelles of CTAF is shown to be due to the combined effects of a more favourable exchange constant in CTAF than in CTAB, slightly different rates of reaction within the two micelles and different values of β, the fraction of micellar head groups neutralized in CTAF and in CTAB.

In both micelles the magnitude of catalysis depends on the charge produced in the intermediate complex and the presence of electron-withdrawing groups to stabilize that charge. Strongest catalysis was found for a reaction leading to a monoanionic intermediate complex in which the charge was stabilized by two nitro groups, and the weakest catalysis was found for a reaction leading to a dianionic intermediate in which no electron-withdrawing groups were present.

INTRODUCTION

On the basis of the pseudophase ion-exchange (PPIE) model of micellar catalysis, the observed rate constants for reactions in the presence of micelles are dependent[1-4] firstly on the binding constant of the substrate to the micelle, K_s, secondly on the exchange constant of the nucleophilic ion (hydroxide ion in this case) and the micellar counterion (X^-), i.e. $K^{OH/X}$, and thirdly on the actual rate of reaction within the micellar pseudophase, k_2^M.

Previous studies[5,6] have shown that many hydrolytic reactions including nucleophilic aromatic substitution and amide and ester hydrolyses occur slightly faster in the presence of micelles of cetyltrimethylammonium fluoride (CTAF) than in the presence of micelles of cetyltrimethylammonium bromide (CTAB). This was not unexpected since the exchange constant for hydroxide/fluoride ($K^{OH/F} = 1 \cdot 0$) is much more favourable[7,8] than that for hydroxide/bromide ($K^{OH/Br} = 10$–20), leading to a higher concentration of hydroxide ions in the micellar pseudophase for micelles of CTAF than

for micelles of CTAB. Surprisingly, however, these reactions in CTAF are only slightly faster (typically two- to threefold) than those in CTAB. The large difference in the relevant exchange constants led us to expect a much larger difference in the observed catalysis by CTAF compared with that by CTAB. In an attempt[1-4] to determine the best values of the above parameters, several workers have reported the use of computer methods to simulate the variation of the observed rate of reaction with changing detergent concentration on the basis of the PPIE model. However, attempts to use this model for reactions in the presence of CTAF have generally not been very successful, primarily because one of the basic assumptions of the PPIE model is that the value of β, the fraction of micellar head groups neutralized, is constant and independent of the CTA concentration. However, for micelles containing hydrophilic counterions, e.g. CTAF, it has recently been shown that β varies significantly for different CTA concentrations.[9,10] As an alternative to the pseudophase ion-exchange model, the pseudophase

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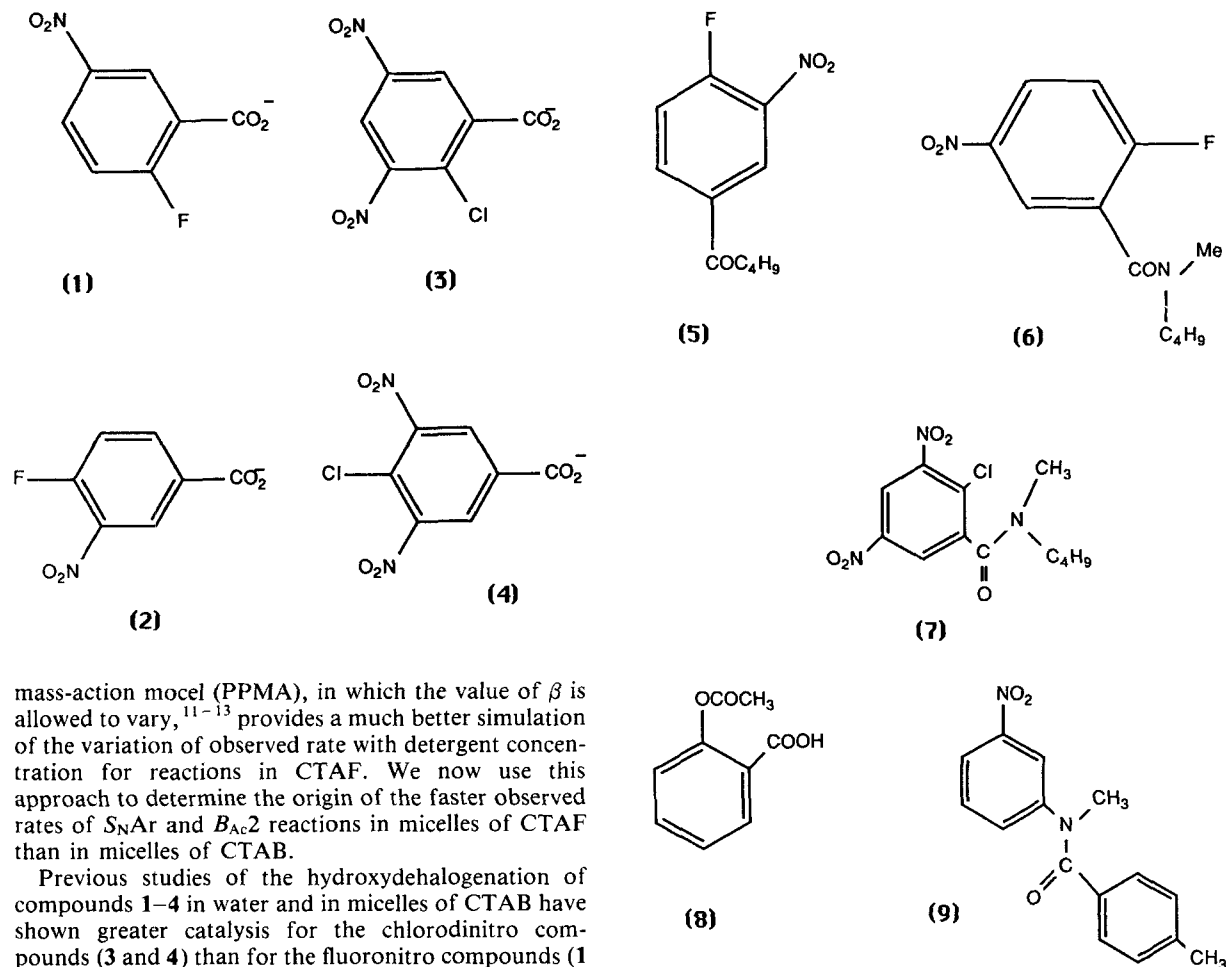
mass-action mocel (PPMA), in which the value of β is allowed to vary,[11-13] provides a much better simulation of the variation of observed rate with detergent concentration for reactions in CTAF. We now use this approach to determine the origin of the faster observed rates of S_NAr and $B_{Ac}2$ reactions in micelles of CTAF than in micelles of CTAB.

Previous studies of the hydroxydehalogenation of compounds 1–4 in water and in micelles of CTAB have shown greater catalysis for the chlorodinitro compounds (3 and 4) than for the fluoronitro compounds (1 and 2). In all of these reactions for compounds 1–4 a double negative charge is produced in the intermediate. Such reactions are susceptible to changes in the polarity of the environment.[14] Transfer from water to CTAB results in a reduction in the polarity[15] and hence of the ion-solvating power of the environment. This leads to weaker catalysis of such reactions by CTAB than is observed for reactions in which charge is not concentrated in the rate-determining step, e.g. reactions in which monoanionic intermediates are produced. This unfavourable effect is offset to some extent for the dinitro compounds (3 and 4) by the presence of two electron-withdrawing nitro groups to stabilize the double negative charge. Hence greater catalysis is observed for these compounds than for the fluoronitro compounds (1 and 2) which possess only one nitro group each to stabilize the double negative charge. We now compare reactions producing a single negative charge (e.g. the hydrolysis of 5, 6 and 7) with those producing a double negative charge (e.g. the hydrolysis of 2) in micelles of CTAB and CTAF. We have also inves-

tigated the $B_{Ac}2$ hydrolyses of aspirin (8) and the anilide 9 in the presence of micelles of CTAF and CTAB. The basic hydrolysis of aspirin also involves the production of a dianionic intermediate because, like substrates 1–4, the carboxylic acid group of aspirin is ionized in basic solution. The hydrolysis of the anilide 9 involves the production of a monoanionic intermediate.

RESULTS AND DISCUSSION

Second-order rate constants for the hydroxydehalogenation of 2, 5, 6 and 7 and for the $B_{Ac}2$ hydrolysis of 8 and 9 in CTAF are given in Table 1 and those for the reaction of 5–7 and 9 in CTAB in Table 2. The second-order rate constants for the hydroxydehalogenation of 2 and for the hydrolysis of 8 in micelles of CTAB are taken from the literature.[4,16] For each compound in both micelles the rate CTA profile showed the typical behaviour of second-order reactions, with the observed

rate first increasing as the CTA concentration was increased and then decreasing with further increase in CTA concentration.

The kinetic data in Tables 1 and 2 were subjected to computer simulation. Rate vs detergent concentration curves predicted by the pseudophase models (PPIE and PPMA) were fitted to the experimental results to deter-

mine the best values of the substrate binding constant, K_s, the second-order rate constant for the reaction in the micellar pseudophase, k_2^M, and the exchange constant (PPIE) or binding constants (PPMA) for the counterions. These results are given in Table 3. For either model, the observed second-order rate constant is given by

$$k_2 = \frac{k_2^W + (k_m K_s - k_2^W) m_{OH} [cta]_m / [OH^-]}{1 + K_s [cta]_m} \quad (1)$$

where k_2^W is the second-order rate constant for the

Table 1. Second-order rate constants $[10^3 \times k_2 \, (l \, mol^{-1} s^{-1})]$ for the reactions of **2** and **5–9** in micelles of CTAF

[CTAF] (mM)	2	5	6	7	8	9
0	2·50	2·87	0·165	18·4	809	1·65
0·1	2·65	—	—	19·8	748	—
0·338	—	11·3	—	—	—	3·35
0·5	3·82	—	—	19·6	823	—
1·0	5·37	—	—	285	1400	—
1·69	—	320	3·10	—	—	9·54
2·0	6·82	—	—	991	3330	—
3·38	—	540	7·95	—	—	67·2
4·0	7·86	554	—	2470	3900	—
8·0	8·23	597	—	3960	3860	107
10·0	8·57	—	16·8	—	—	—
12·0	—	—	—	4370	3480	—
13·5	—	554	17·3	—	—	104
16·0	—	535	17·4	4340	2960	103
20·0	8·26	—	17·5	4240	2740	93·7
33·8	—	405	16·3	—	—	76·1
36·0	—	—	—	3590	—	—
40·0	7·47	—	—	—	1810	—
50·7	—	340	13·7	—	—	59·3
67·6	—	294	12·2	—	—	53·1
84·5	—	245	11·4	—	—	49·6
101	—	221	10·3	—	—	44·1
118	—	205	9·43	—	—	40·4
135	—	189	8·98	—	—	35·8
[OH] (mM)	100	20	20	10	10	4·7
$T(^\circ C)$	56·7	19·5	56·7	74·0	56·4	71·0

Table 2. Second-order rate constants $[10^3 \times k_2 \, (l \, mol^{-1} s^{-1})]$ for the reactions of **5–7** and **9** in micelles of CTAB[a]

[CTAB] (mM)	5	6	7	9
0	2·87	0·165	18·4	1·65
0·1	2·83	—	20·3	3·21
0·5	66·3	0·415	20·6	3·39
1·0	202	1·46	177	3·50
2·0	—	—	1170	49·5
3·0	—	—	—	80·7
4·0	—	—	2610	—
5·0	244	7·72	—	95·8
7·0	—	—	—	114
8·0	—	—	3120	—
10·0	197	9·92	—	92·5
12·0	—	—	3175	—
15·0	164	9·75	—	89·7
20·0	135	9·03	2870	72·6
25·0	121	8·54	—	69·1
28·0	—	—	2540	—
30·0	109	7·69	—	62·3
36·0	—	—	2250	—
40·0	—	7·16	—	61·9
[NaOH] (mM)	20	20	10	4·7
$T(^\circ C)$	19·5	56·7	74·0	71·0

[a] Rate constants for reactions of **2** and **8** in CTAB are in Refs 4 and 16, respectively.

Table 3. Derived kinetic data for the reactions of **2** and **5–9** in the presence of micelles

Parameter	Micelle	2	5	6	7	8	9
K_s	CTAB	731	753	88	82	491	150
	CTAF	921	864	93	112	1423	207
$10^3 \times k_2^W$ ($l \, mol^{-1} s^{-1}$)		—	2·50	2·87	0·165	18·4	809	1·65
$10^3 \times k_2^M$ ($l \, mol^{-1} s^{-1}$)	CTAB	0·266	2·80	0·27	72·8	26·5	1·39
	CTAF	0·16	4·7	0·24	46·5	21·4	0·85
Increase in CTAF (%)		−40	68	−11	−36	−19	−39
Observed catalysis	CTAB	2·6	85	60	172	2·4	69
	CTAF	3·4	208	105	236	4·8	65
Increase in CTAF (%)		31	145	75	37	100	33
k_2^M / k_2^W	CTAB	0·11	0·98	1·64	3·96	0·033	0·84
	CTAF	0·06	1·64	1·45	2·53	0·026	0·52

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Substrate 5. Reaction in CTAB micelles

PPIE curve - solid line : cmc=0.3mM beta=0.8 KOHBr=10.0 Ks=753 km=0.0195
PPMA curve - broken line : cmc=0.3mM KOH=55 KBr=550 Ks=1270 km=0.0189

Substrate 5. Reaction in CTAF micelles

PPIE curve - solid line : cmc=1.0mM beta=0.3 KOHF=0.727 Ks=704 km=0.0640
PPMA curve - broken line : cmc=1.0mM KOH=55 KF=40 Ks=864 km=0.0332
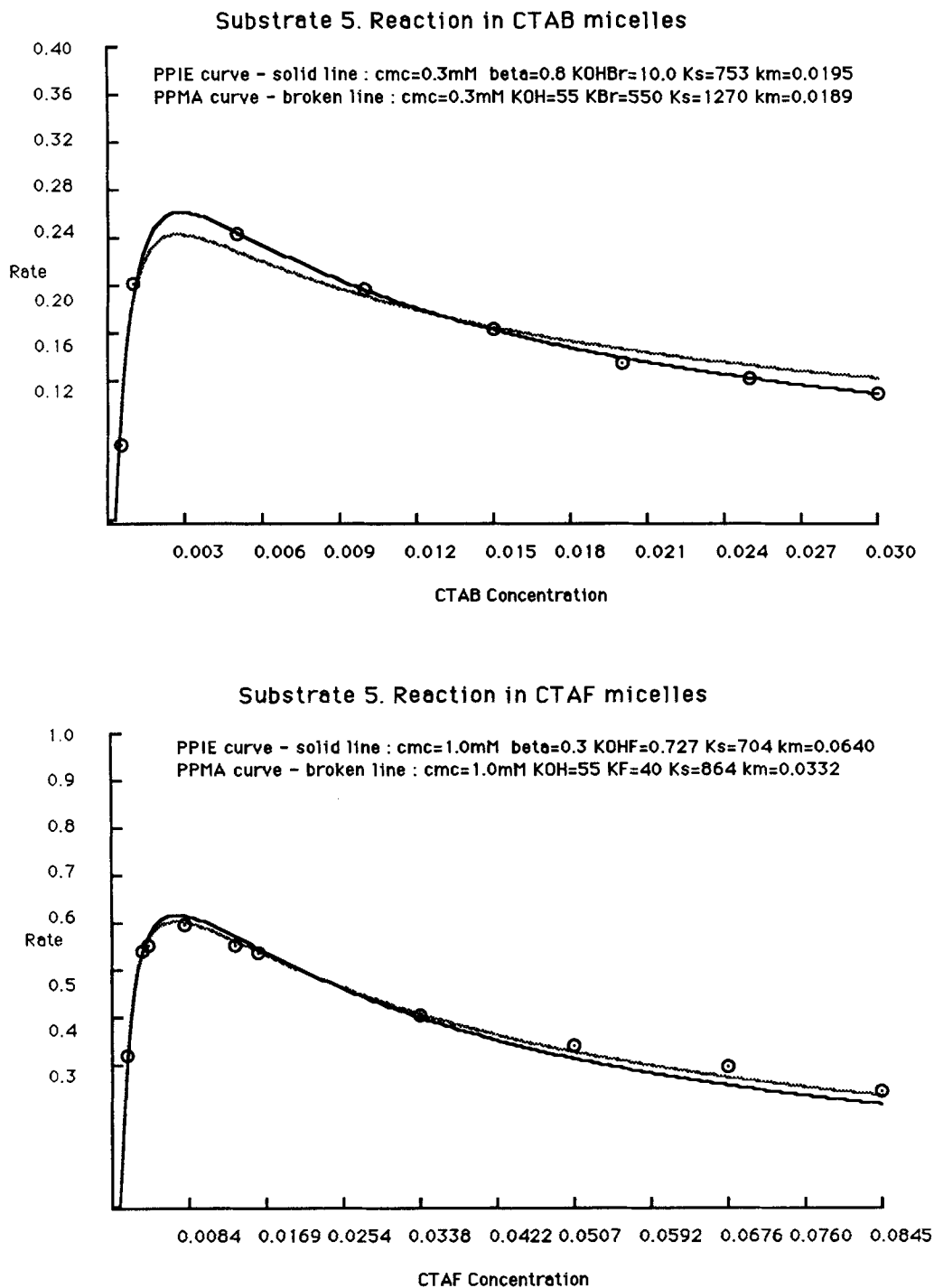
Figure 1. Variation of second-order rate constant $(l\,mol^{-1}\,s^{-1})$ with CTA concentration (M) for the hydroxydehalogenation of 5 in CTAB (top) and in CTAF (bottom). The curves are predicted from the parameters in Table 3 using the PPIE model (solid lines) [equations (1) and (2)] and the PPMA model (broken lines) [equations (1) and (3)]

reaction in the aqueous phase (taken as being identical with that measured for the reaction in the absence of detergent) and $[cta]_m$ is the concentration of micellized detergent. It is assumed that if the detergent concentration is sufficient for micelles to form, $[cta]_w$ is always equal to the critical micelle concentration (c.m.c.), and hence $[cta]_m = [cta] - c.m.c.$ Finally, m_{OH} is the fraction of hydroxide counterions present in the Stern layer, expressed relative to the total number of cta head groups.

In the PPIE model,[1-4] it is assumed that a constant fraction, β, of the head groups have counterions present, and that hydroxyl and bromide ions compete for the sites in an ion exchange equilibrium governed by

$$K^{OH}_{Br} = \frac{m_{Br}[OH^-]_w}{m_{OH}[Br^-]_w}$$

This leads to the equation

$$m^2_{OH}(K^{OH}_{Br} - 1)[cta]_m + m_{OH}$$
$$\times \{[OH^-] + K^{OH}_{Br}[Br^-] - \beta(K^{OH}_{Br} - 1)[cta]_m\}$$
$$- \beta[OH^-] = 0 \quad (2)$$

In the PPMA model,[11-13] it is assumed rather that the two anions present compete independently for the available counterion sites. For each anion present, an equilibrium constant for binding into the Stern layer is defined by

$$K^A = [A^-]_w(1 - \beta)/m_A$$

On this occasion, β is treated as a variable equal to $m_{OH} + m_F$.

As an alternative to equation (2), the following pair of equations are obtained, which must be solved iteratively:

$$m_F = 1 - m_{OH} - \frac{K^{OH}m_{OH}}{[OH^-] - [cta]_m m_{OH}} \quad (3a)$$

$$m_{OH} = 1 - m_F - \frac{K^F m_F}{[F^-] - [cta]_m m_F} \quad (3b)$$

The parameter k_m used in these treatments is the second-order rate constant for the reaction in the micellar pseudophase, given by

$$Rate_m = k_m \frac{[S]_m[OH]_m}{[cta]_m}$$

The term $[OH]_m$ refers to the molar concentration of hydroxide ion relative to the total volume of solution. To obtain a second-order rate constant characteristic of the micelle phase suitable for direct comparison with k^W_2, the hydroxide ion concentration should rather be related to the volume of the Stern layer.[3]

k^M_2 is defined by

$$Rate_m = k^M_2[OH]^{true}_m[S]_m$$

and obtained from

$$k^M_2 = k_m V_{cta}$$

since

$$[OH]^{true}_m = \frac{[OH]_m}{[cta]_m V_{cta}}$$

where V_{cta} is the molar volume of the Stern layer,[2] taken as $0.14\ dm^3 mol^{-1}$.

In line with previously reported results[2] for the PPIE model, a unique set of parameters was not obtained since the values of the exchange constant $K^{OH/Br}$ and the second-order rate constant in the micelle, k^M_2, are compensatory. A good fit could be obtained with a number of combinations of these parameters. We found a good fit with $K^{OH/Br} = 10$ in all cases. As reported,[17,18] a value of $K^{OH/BR} = 2$ has previously been used for 8, but we found an equally good fit with $K^{OH/Br} = 10$ and this value is closer to the range of $K^{OH/Br}$ values reported for most compounds studied.[2] For the PPMA model we used 40 and 55 $l mol^{-1}$ as the binding constants of fluoride[13] and hydroxide,[11] respectively. This is equivalent to an exchange constant $K^{OH/F} = 0.73$, which is similar to that reported by Bartet et al.[8] for these anions.

As suggested by Tanford,[19] we used the kinetic c.m.c. value that gives the best fit for each substrate rather than a single literature value. For CTAB we used c.m.c. $= 3 \times 10^{-4}$ M for 2 and 5 and 9×10^{-4} M for 6–9. For CTAF we used c.m.c. $= 1 \times 10^{-3}$ M all compounds except 9, for which we used 1.5×10^{-3} M, and 2, for which we used 3×10^{-4} M. For 5, an example of the fit obtained by the two models is shown in Figure 1. It can be seen that the best fit of the experimental data is obtained using the PPIE model in CTAB and the PPMA model in CTAF.

CTAF versus CTAB

The observed catalysis at the optimum CTA concentration ranged from 2.6 (2) to 85 (5) in CTAB and to as large as 236 (7) in CTAF. With the exception of 8, similar binding constants were obtained in both micelles for each of the substrates studied. Factors leading to efficient solubilization of a substrate by a micelle include the presence of hydrophobic groups, long alkyl chains or nitro groups, on the substrate and the electrostatic attraction between the positive charge on the micelle and negatively charged substituents (e.g. carboxylate groups) on the substrate. In the case of aspirin (8), no hydrophobic alkyl or nitro groups are present and the only factor which assists solubilization by the micelle is the electrostatic attraction between the positive micelle and the negative carboxylate group. Hence for this compound we observe a larger K_s value in micelles of CTAF than in micelles of CTAB, possibly because of the smaller β value in CTAF and hence the

larger charge on the micelle in that case. For all of the other substrates hydrophoibic butyl chains (**5–7**) and/or nitro groups (**2, 5–7** and **9**) lead to efficient solubilization by the micelles and hence we do not see large differences in the K_s values in CTAB and CTAF for these substrates.

The greater observed catalysis in CTAF was primarily a result of the more favourable exchange constant for hydroxide/fluoride than for hydroxide/bromide. However, this difference was modified by two other effects, first by the slightly different rate constants in micelles of CTAF and CTAB and second by the different β values in the two micelles.[10] For example, at 4 mM CTA for CTAF, $\beta = 0.3$, whereas for CTAB, $\beta = 0.8$. Thus, in CTAF, despite having a more favourable ratio of hydroxide and fluoride, there is a smaller total concentration of counterions present on the micelles than in micelles of CTAB.

On comparing the percentage change in k_2^M on transfer from CTAB to CTAF (Table 3) with the percentage increase in the observed catalysis in the two micelles (Table 3), we find that for **2, 7** and **9** a 30–40% decrease in k_2^M in CTAF still results in slightly greater observed catalysis (31–37%) by CTAF, presumably because the increase in hydroxide concentration in micelles of CTAF compared with micelles of CTAB is more important than the decrease in k_2^M. For **8**, a 19% decrease in k_2^M in CTAF resulted in doubling of the observed catalysis. For **6** a smaller decrease (11%) in k_2^M in CTAF resulted in a significant increase in the observed catalysis (75%) in CTAF compared with CTAB. For **5**, an increase (68%) in k_2^M in CTAF resulted in a large increase (145%) in the observed catalysis on transfer from CTAB to CTAF.

Monoanionic versus dianionic intermediates

For both micelles high catalysis was observed for the reactions of **5, 6, 7** and **9**, for which monoanionic intermediates were produced. In comparison, the reaction of **2** and **8**, for which dianionic intermediates were produced, showed only low catalysis. These differences in the magnitude of catalysis for reactions involving mono- and dianionic intermediates are a result of differences in the k_2^M/k_2^W rate ratios for the reactions of these compounds, presumably because reactions which involve dianionic intermediates are hindered by a reduction in the polarity of the environment on transfer from water to the micelle, as predicted by the Hughes–Ingold solvent theory.[14] It is of interest that a direct correlation exists between the charge formed on the intermediate, the number of nitro groups available to stabilize that charge and the magnitude of the catalysis as shown by the k_2^M/k_2^W rate ratios. For example, the smallest k_2^M/k_2^W rate ratio (0·03–0·04) is observed for the reaction of **8**, with a double negative charge on the intermediate and no nitro groups to stabilize it. A

slightly higher k_2^M/k_2^W rate ratio (0·06–0·11) is observed for the reaction of **2**, with a double negative charge on the intermediate and one nitro group to stabilize it. For **5, 6** and **9**, the k_2^M/k_2^W rate ratio is higher (0·5–1·6), with a single negative charge on the intermediate and one nitro group to stabilize it. Finally, for **7** the k_2^M/k_2^W rate ratio is the highest observed (2·5–4·0), with a single negative charge on the intermediate and two nitro groups to stabilize it.

EXPERIMENTAL

Materials. 1-(4′-Fluoro-3′-nitrophenyl)-1-pentanone **5** (found, C 58·4, H 5·1, N 6·4; $C_{11}H_{12}FNO_3$ requires C 58·7, H 5·3, N 6·2%) was prepared in 67% yield by the Friedel–Crafts acylation ($AlCl_3$ catalyst in CS_2 solvent) of fluorobenzene followed by nitration with a mixture of fuming nitric acid and concentrated sulphuric acid at −20 to −25 °C. After chromatography (CH_2Cl_2/silica) using a Chromatotron the compound was pure by TLC. Compounds **1, 2, 8** and **9** were available from previous work.[4,16,20]

N-Methyl-N-butyl-2-fluoro-5-nitrobenzamide (**6**) (found, C 56·3, H 5·9, N 10·9; $C_{12}H_{15}FN_2O_3$ requires C 56·7, H 5·9, N 11·0%) was obtained as a yellow oil from the reaction of N-methylbutylamine with 2-fluoro-5-nitrobenzoyl chloride in dry acetone at 56 °C (40 min). The product of the reaction was obtained by methylene chloride extraction of the reaction mixture after pouring into water. The oil was pure by TLC and the NMR spectrum was consistent with the expected product.

N-Methyl-N-butyl-2-chloro-3,5-dinitrobenzamide (**7**) (found, m/z 315·0624; $C_{12}H_{14}ClN_3O_5$ requires m/z 315·0622) was obtained as a yellow oil, pure by TLC (SiO_2/CH_2Cl_2) from the reaction of N-methylbutylamine with 2-chloro-3,5-dinitrobenzoyl chloride in acetone at 56 °C for 40 min. The product was isolated as described above for **6**.

CTAB was purified by the method of Mukerjee and Mysels.[21] CTAOH was prepared as described previously.[22] CTAF was prepared by the neutralization of CTAOH with HF in a plastic beaker. The resulting solution was shown to be neutral (glass electrode) and contained no detectable silver ions. The fluoride concentration was determined using a fluoride ion-selective electrode by comparison with standard sodium fluoride solutions. Microanalyses were performed by the Australian Microanalytical service.

Distilled water was further purified by a Millipore system to achieve a resistivity of 16 MΩ cm.

Kinetics. Stock solutions of the substrates 0·01 M in analytical-reagent grade acetonitrile), CTAB and CTAF (0·05 or 0·192 M in water) and sodium hydroxide (1·0 M in water) were prepared. The CTAF was stored

in plastic containers. Sodium hydroxide was standardized by titration against hydrochloric acid with bromocresol green as indicator. The required amounts of detergent solution (CTAB or CTAF) and sodium hydroxide were pipetted into a cuvette and the solution was allowed to reach thermal equilibrium. The substrate (18 μl) was then added by microsyringe, the mixture was stirred vigorously and product formation was monitored at 415 nm (2), 310 nm (5), 400 nm (6), 363 nm (7), 297 nm (8) and 233 nm (9) on either a Varian DMS 70 or a model 635 UV–visible spectrophotometer. The reactions were followed for ten half-lives where practical to obtain an experimental infinity measurement. For slow reactions data were collected over at least two half-lives. A computer program designed to give the best straight-line fit was used to provide an infinity value. Good agreement was obtained between rate constants obtained by the two methods. Reactions were carried out in a cuvette maintained at constant temperature in the jacketed cell holder of the spectrophotometer. The temperature within the cell was determined with a Jenco Thermistor thermometer.

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