of product(s) (Scheme I). Analysis of the crude reaction mixture also indicated the absence of carbonyl-containing compounds, and no thallium adducts could be detected in, or isolated from, the reaction mixture.

Experimental Section

Melting points were taken on a Koeffler hot-stage microscope and are uncorrected. IR spectra were recorded on a Perkin-Elmer 237 spectrophotometer. NMR spectra were recorded in $CDCl_3$ on a Varian XL-200 spectrometer. ^1H NMR spectra were obtained at 200 MHz, and ^{13}C NMR spectra were obtained at 50.3 MHz. Chemical shifts are reported in parts per million downfield from Me_4Si. Low-resolution mass spectra were performed on an A.E.I. MS9 spectrometer operating at a probe temperature of 250 °C. Microanalyses were conducted by Mr. M. Hart, Department of Chemistry, Manchester University, Manchester, U.K.

5,6-Benzobicyclo[2.2.1]hept-5-ene-2-*exo*,7-*anti*-diyl Dinitrate (8). Addition of thallium(III) nitrate (12.4 g, 0.028 mol) in methanol (30 mL) to a stirred solution of 2 (4.0 g, 0.028 mol) in methanol (30 mL) gave an immediate precipitate of thallium(I) nitrate which was removed by filtration and the filtrate added to a 2 N solution of sulfuric acid (100 mL). The acidic solution was shaken for 5 min and extracted with ether (3 × 50 mL), and the combined ether extracts were washed with saturated $NaHCO_3$ solution (3 × 50 mL). The ether layer was filtered and evaporated to dryness to give a viscous yellow oil (6.75 g), which was subjected to column chromatography through silica gel (35–65 mesh, 100 g) with chloroform as eluent. An initial band was obtained as a gum after evaporation of solvent, which was crystallized from diethyl ether–petroleum ether (bp 30–40 °C) to afford 8 as a white crystalline product (2.83 g, 38%): mp 100–101 °C; ν_{max} (Nujol) 1660, 1638, 1280, 1290, 1300, 1305 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 32.7 (C-3), 44.8 (C-4), 50.0 (C-1), 83.0 (C-2), 88.5 (C-7), 123.7 (C-11), 128.0 (C-9), 128.7 (C-10), 137.1 (C-5), 142.7 (C-6); MS, *m/e* 220 ($M - NO_2$), 204, 158, 131 (base). Anal. Calcd for $C_{11}H_{10}O_6N_2$: C, 49.62; H, 3.76; N, 10.53. Found: C, 49.71; H, 3.82; N, 10.34.

2-*exo*-Methoxy-5,6-benzobicyclo[2.2.1]hept-5-en-7-*anti*-yl Nitrate (9). A second homogeneous fraction was obtained on further elution of the above silica gel chromarographic column with chloroform, which crystallized from petroleum ether (40–60 °C) and afforded 9 as a white crystalline product (2.72, 41.1%); mp 55–56 °C; IR ν_{max} (Nujol) 1650, 1630, 1295, 1284 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 33.4 (C-3), 44.8 (C-4), 49.9 (C-1), 57.2 (OCH_3), 82.0 (C-2), 89.5 (C-7), 121.8 (C-8), 123.0 (C-11), 127.3 (C-10), 127.7 (C-9), 139.5 (C-5), 143.4 (C-6); MS, *m/e* 204 ($M - OCH_3$), 189, 129 (base). Anal. Calcd for $C_{12}H_{13}O_4N$: C, 61.30; H, 5.33; N, 5.95. Found: C, 61.52; H, 5.70; N, 5.93.

Crystal Structure Determination of 5,6-Benzobicyclo[2.2.1]hept-5-ene-2,7-diyl Dinitrate (8). Slow evaporation of a chloroform solution of 8 produced crystals belonging to the monoclinic space group C_{2h}^6—$C2/c$ with a = 24.100 (4) Å, b = 6.990 (2) Å, c = 17.524 (3) Å, and β = 129.07 (2)° at 22 °C and Z = 8. The calculated density is 1.543 $g{\cdot}cm^{-3}$. Of the 2621 unique reflections measured with Mo Kα radiation ($2\theta_{max}$ = 55°) on an Enraf-Nonius CAD4/F diffractometer, 2101 having $F_o^2 \geq 3\sigma(F_o^2)$ were included in the final refinement. There was no important absorption or decomposition. In the final full-matrix least-squares refinement cycles the C, N, and O atoms were refined with anisotropic, and the H atoms with isotropic, thermal parameters; final agreement factors R and R_w on F_o are 0.034 and 0.046 for 213 variables. All C–H bond lengths fall in the range 0.91–0.99 Å. The ten largest peaks (height <0.26 $e{\cdot}Å^{-3}$) in the final difference Fourier map are located at the centers of C–C bonds; the deepest trough (–0.20 $e{\cdot}Å^{-3}$) is near the center of the aromatic ring. The structure is illustrated in Figure 2 in the supplementary material; H–C–C–H dihedral angles are given in Table I, together with observed hydrogen coupling values from the NMR analysis.

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Registry No. 2, 4453-90-1; 8, 98875-84-4; 9, 98875-85-5; thallium(III) nitrate, 13746-98-0.

Supplementary Material Available: Tables of refined atomic positional and thermal parameters, selected bond lengths and angles, and observed and calculated structure factor amplitudes for 8 and autocorrelated two-dimensional 200-MHz ^1H NMR contour plot of 8 and perspective drawing of the molecular structure of 8 (19 pages). Ordering information is given on any current masthead page.

Indicator Deprotonation in Micelles of a Hydroxyethyl Surfactant

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Functionalized surfactants can generate micelles which are effective nucleophilic or basic reagents.[2-4] In many systems reaction involves attack of an oximate, hydroxamate, alkoxide, or thiolate residue formed by deprotonation of a weak acid, so that reaction rates are pH dependent. The variation of the overall rate constant with pH can be used to calculate an apparent equilibrium constant for deprotonation of the weakly acidic functional group.[3,5]

Deprotonation of indicators in solutions of cationic micelles can be treated quantitatively by calculating the concentration of OH^- bound to the micelle and the distribution of the indicator between the micellar and aqueous pseudophases.[6,7] For a system containing OH^- and surfactant counterion the concentration of micellar bound OH^- can be calculated in terms of the ion-exchange model. This treatment has been applied successfully to deprotonations of areneimidazoles,[8] nitroindoles,[9] and phenols, based on some simplifying assumptions.[10,11] It readily explains how deprotonation of a weakly acidic group at a micellar surface follows not the total concentration of OH^- but that at the surface of the micelle and, for a given [OH^-], decreases with increase of [surfactant] or addition of salt. A similar approach has been applied to micellar rate effects.[4,6,7,13]

The extents of deprotonation of weakly acidic groups of functional micelles seem to follow the total amount of OH^-, as given stoichiometrically,[5] or by the measured pH if buffers are used,[3] whereas the ion-exchange model predicts that the determining factor should be the amount of OH^- at the micellar surface.[6-8] We have investigated

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(2) Südholter, E. J. R.; van de Langkruis, C. B.; Engberts, J. B. F. N. *Recl: J. R. Neth. Chem. Soc.* **1980**, *99*, 73.

(3) Fornasier, R.; Tonellato, U. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1301.

(4) Bunton, C. A.; *Catal. Rev. Sci. Eng.* **1979**, *20*, 1.

(5) (a) Bunton, C. A.; Ionescu, L. G. *J. Am. Chem. Soc.* **1973**, *95*, 2912. (b) Bunton, C. A.; Diaz, S. *Ibid.* **1976**, *98*, 5663. (c) Biresaw, G.; Bunton, C. A.; Quan, C.; Yang, Z.-Y. *Ibid.* **1984**, *106*, 7178.

(6) Romsted, L. S. In "Surfactants in Solution"; Mittal, K. L., Lindman, B., Ed.; Plenum Press: New York, 1984; Vol. 2, p 1015.

(7) Quina, F. H.; Chaimovich, H. *J. Phys. Chem.* **1979**, *83*, 1844.

(8) Bunton, C. A.; Hong, Y. S.; Romsted, L. S. In "Solution Behavior of Surfactants"; Mittal, K. L., Fendler, E. J., Eds.; Plenum Press: New York, 1982; Vol. 2, p 1137.

(9) (a) Cipiciani, A.; Savelli, G.; Bunton, C. A. *J. Phys. Chem.* **1983**, *87*, 5259. (b) Cipiciani, A.; Germani, R.; Savelli, G.; Bunton, C. A. *J. Chem. Soc., Perkin Trans. 2* **1985**, 527.

(10) Bunton, C. A.; Romsted, L. S.; Sepulveda, L. *J. Phys. Chem.* **1980**, *84*, 2611.

(11) It was originally assumed that areneimidazolide ions are bound quantitatively to cationic micelles. This assumption is not strictly correct for solutions containing high concentrations of added salts.[12]

(12) Romsted, L. S. *J. Phys. Chem.*, in press.

(13) van de Langkruis, G. B.; Engberts, J. B. F. N. *J. Org. Chem.* **1984**, *49*, 4152.

0022-3263/85/1950-5374$01.50/0 © 1985 American Chemical Society

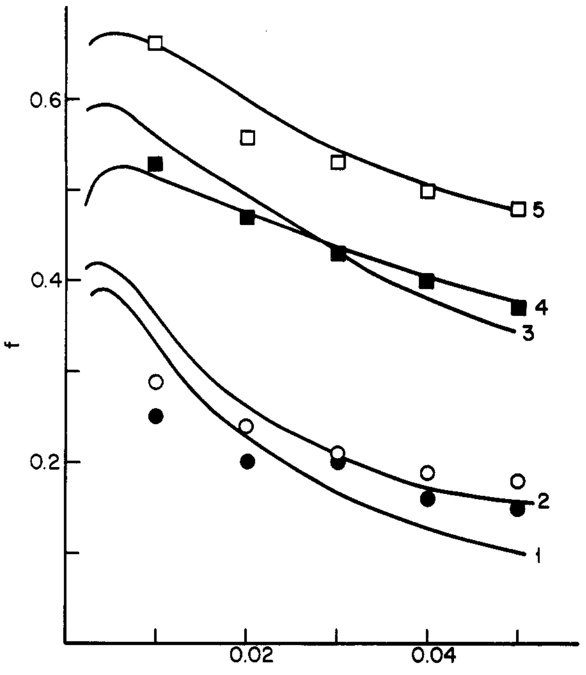
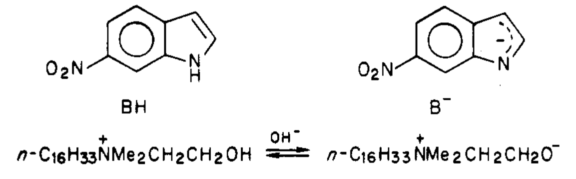


Figure 1. Extent of deprotonation of 5-nitroindole in micelles of 1 and comicelles of 1 and CTABr. The closed points relate to micelles and the open points to comicelles: ●, ○ in 0.01 M NaOH, ■, □ in 0.1 M NaOH. The lines are calculated by using the parameters in Table I.

this problem by determining extents of deprotonation of 5-nitroindole (BH) in solutions of hexadecyl (2-hydroxyethyl)dimethylammonium bromide (1).



BH B⁻

1 1a

In water the estimated pK_a of 5-nitroindole is 14.75,[14] and the apparent pK_a of micellized 1 is ca. 12.3, estimated kinetically.[5] For the nonmicellizing model compound, choline, pK_a = 12.8.[15]

We also examined deprotonation of 5-nitroindole-2-carboxylate ion,[9b] but we did not attempt to treat its deprotonation in solutions of 1 quantitatively.

Experimental Section

Materials. The preparation and purification of the indicators and surfactants have been described.[5,9]

Deprotonation. The fraction, *f*, of deprotonated 5-nitroindole was estimated spectrophotometrically at 25.0 °C from the absorbance at 398 nm, with 8.75×10^{-5} M indicator.[9a] Deprotonation of 5-nitroindole-2-carboxylate ion in CTABr was estimated from absorbance at either 387 or 393 nm and the two sets of values of *f* agree.[9b] However, values of *f* for 5-nitroindole-2-carboxylate ion in 1 obtained at these two wavelengths differed.

Results and Discussion

The variation of the fraction, *f*, of deprotonation of 5-nitroindole (BH) is shown in Figure 1. The total concentration of NaOH was 0.01 or 0.1 M, and we used both micelles of 1 and comicelles of it with cetyl trimethylammonium bromide (CTABr). The comicelles contained a tenfold excess of CTABr over 1.

Deprotonation in micelles of CTABr was treated quantitatively by estimating distribution of the nonionic indicator using eq 1,[6,8-10] where subscripts M and T denote

$$\frac{[\mathrm{BH_M}]}{[\mathrm{BH_T}]} = \frac{K_\mathrm{S}[\mathrm{D_n}]}{1 + K_\mathrm{S}[\mathrm{D_n}]} \qquad (1)$$

micellar bound and total material, respectively, the concentration of micellized surfactant, $[\mathrm{D_n}]$, is the total concentration less the critical micelle concentration, cmc, and K_S is a binding constant written in terms of micellized surfactant.

The basicity constant in the micellar pseudophase is written as[6,8-10]

$$K_\mathrm{B}{}^\mathrm{M} = \frac{[\mathrm{BH_M}]m_{\mathrm{OH}}{}^\mathrm{s}}{[B_\mathrm{M}{}^-]} \qquad (2)$$

where

$$m_{\mathrm{OH}}{}^\mathrm{s} = [\mathrm{OH^-{}_M}]/[\mathrm{D_n}]^6 \qquad (3)$$

and for a mixture of counterions

$$m_{\mathrm{OH}}{}^\mathrm{s} + m_{\mathrm{Br}}{}^\mathrm{s} = \beta \qquad (4)$$

where β is the degree of counterion binding to the micelles and is assumed to be constant for nonfunctional micelles.[6] Deprotonation of a functional micelle should decrease β, and we write the effective value, β', in terms of β_0, in absence of deprotonation, and $m_0{}^\mathrm{S}$, where $m_0{}^\mathrm{S}$ is the mole ratio of deprotonation of the hydroxy group of 1 to total surfactant, i.e.,

$$\beta' = \beta_0(1 - m_0{}^\mathrm{S}) \qquad (5)$$

We calculated $m_0{}^\mathrm{S}$ from the extent of deprotonation estimated kinetically.[5] The correction is very small for comicelles of 1 and CTABr with the latter in tenfold excess.

The interionic competition for the micelle or comicelle is given by

$$K_{\mathrm{Br}}{}^{\mathrm{OH}} = [\mathrm{OH^-{}_W}][\mathrm{Br^-{}_M}]/([\mathrm{OH^-{}_M}][\mathrm{Br^-{}_W}]) \qquad (6)$$

The value of $m_{\mathrm{OH}}{}^\mathrm{S}$ can then be calculated from eq 7 in terms of assumed values of β_0 and $K_{\mathrm{Br}}{}^{\mathrm{OH}}$.[6,8,9]

$$(m_{\mathrm{OH}}{}^\mathrm{S})^2 + m_{\mathrm{OH}}{}^\mathrm{S}\left(\frac{[\mathrm{OH^-{}_T}] - K_{\mathrm{Br}}{}^{\mathrm{OH}}[\mathrm{Br^-}]}{[D_n](K_{\mathrm{Br}}{}^{\mathrm{OH}} - 1)} - \beta'\right) - \frac{[\mathrm{OH^-{}_T}]\beta'}{[\mathrm{D_n}](K_{\mathrm{Br}}{}^{\mathrm{OH}} - 1)} = 0 \qquad (7)$$

In eq 7 $[\mathrm{OH^-{}_T}]$ is added [NaOH] less that consumed by deprotonation of the hydroxyethyl surfactant, estimated kinetically.[5] The correction is small for comicelles.

We attempted to fit the variation of *f* with [surfactant], first taking values of $K_{\mathrm{Br}}{}^{\mathrm{OH}} \approx 15$ and $\beta_0 \approx 0.78$ because they fitted deprotonation in CTABr with $K_\mathrm{B}{}^\mathrm{M} \approx 0.15$.[9a,16] We could not get good agreement among all observed and calculated values of *f* using these parameters. For experiments in 0.01 M NaOH the decrease of *f* with increasing [surfactant] was smaller than predicted. We did not use low [surfactant] because changes in the cmc and possibly the extent of substrate binding as the micelle is deprotonated could cause major problems in very dilute surfactant. We took cmc values similar to those in water,[17]

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[14] Yagil, G. *Tetrahedron* **1967**, *23*, 2855.

[15] Haberfield, P.; Pessin, J. *J. Am. Chem. Soc.* **1982**, *104*, 6191.

[16] Values of $K_\mathrm{B}{}^\mathrm{M}$ calculated with concentration of $\mathrm{OH^-}$ written as a mole fraction cannot be compared directly with the classical values in water for which concentration is typically written as molarity. Comparison can be made by writing the concentration of micellar bound $\mathrm{OH^-}$ as a molarity in the micellar pseudophase.[4,6,8-10]

Table I. Attempted Fitting of Variations in f^a

[NaOH]	surfactant	K_S, M^{-1}	β_0	K_{Br}^{OH}	$K_B^{M\,b}$	plot[c]
0.01	1	200	0.75	15	0.05	1
		200	0.75	5	0.12	
		200	0.85	5	0.15	
0.01	1/CTABr[d]	300	0.75	15	0.12 (0.12)	2
		300	0.85	15	0.17	
0.1	1	400	0.75	15	0.025	3
		400	0.75	4	0.06	4
		400	0.85	4	0.08	
0.1	1/CTABr[d]	400	0.75	15	0.14 (0.16)	5

[a] Calculated taking cmc = 6×10^{-4} M except for comicelles in 0.01 M NaOH where cmc = 10^{-3} M. [b] Values in parentheses calculated with constant β. [c] Refers to curves in Figure 1. [d] [1]: [CTABr], 1:10.

but surfactant concentrations are such that the calculations are insensitive to the value of the cmc.

Plots of *f* vs. [surfactant] are shown in Figure 1. They are based on the parameters given in Table I. For deprotonation in 0.1 M NaOH and comicelles of 1 and CTABr the experimental data can be fitted taking values of K_S, K_{Br}^{OH} and K_B^M which are very similar to those used to fit the data in CTABr,[9a] and the fitting is insensitive to variation of β (eq 7). However, for deprotonation in micelles of the hydroxyethyl surfactant 1 we could not fit the data taking values of both K_{Br}^{OH} and K_B^M similar to those which fit the data in CTABr (Figure 1 and Table I).

We were unable to fit the data for deprotonation in 0.01 M NaOH, although the deviations are not large for comicelles of 1 and CTABr. However, for micelles of 1 we could not fit the data even approximately by using parameters similar to those used for data in CTABr, and we had to take a lower than expected value of K_S.[9a] As is often found for experiments in ionic aqueous micelles various combinations of parameters give very similar calculated plots.

The ion-exchange model relies on the value of β,[6] which is subject to uncertainty, because of changes in extent of deprotonation, but the uncertainty should be relatively small for comicelles of 1 and CTABr. There is also uncertainty as to the depletion of OH^- by deprotonation of the hydroxyl group of 1, with formation of **1a**. The alkoxide residue in **1a** should be too weakly basic to deprotonate 5-nitroindole. An additional question is that of micellar binding of the anionic conjugate base of the indicator. Binding to nonfunctional micelles was assumed to be essentially quantitative,[8,9] although this assumption probably fails in relatively concentrated salt solutions. It may also fail as the charge on micellized 1 decreases due to formation of zwitterionic **1a**. Thus our assumption of complete binding of the anion of 5-nitroindole will be least satisfactory at relatively low [1] where there will be most deprotonation of the hydroxy group of the surfactant. However, incomplete binding is not the only source of the discrepancies because if it were they would be most serious at high [NaOH].

It appears that the pseudophase ion-exchange model cannot be applied quantitatively to deprotonation of 5-nitroindole in solutions of micellized 1, although it is qualitatively satisfactory in that it explains the decrease of *f* with increasing [1] and the relatively small increase of *f* with increasing [NaOH].

The pseudophase model of micellar effects upon reaction rates and equilibria is based on the assumption that the micellar reaction takes place in a discrete region adjacent to the ionic head groups, so that the problem is to estimate reactant concentrations in this region.[2-7] Apparently this model cannot be readily applied to a cationic micelle which becomes zwitterionic as the hydroxyl group is deprotonated, and this changing charge distribution is not adequately described merely by a decrease in β.

Table II. Deprotonation of 5-Nitroindole-2-carboxylate Ion[a]

	conditions			
	0.01 M NaOH		0.1 M NaOH	
[*D*], M	1	1/CTABr[b]	1	1/CTABr[b]
0.01	20 (24)	21 (25)	39 (43)	51 (53)
0.02	17 (21)	16 (20)	35 (39)	42 (45)
0.03	15 (20)	15 (19)	32 (36)	38 (41)
0.04	14 (19)	14 (18)	30 (34)	35 (38)
0.05	14 (19)	13 (17)	29 (33)	33 (36)

[a] Values of *f*% estimated from absorbance at 393 nm; values in parentheses are from absorbance at 387 nm. [b] Comicelles of [1]: [CTABr], 1:10.

The extent of deprotonation of 5-nitroindole-2-carboxylate ion decreases, as expected, with increasing [surfactant] but the values depend upon the wavelength used for estimation of *f* (Table II). This problem was not found for experiments with CTABr,[9b] but in solutions containing 1 there is only an ill-defined shoulder in the spectrum of the indicator, whereas it is well-defined in CTABr. Such spectral shifts in micellar solutions are sometimes observed and can be a problem in measurements of acid dissociation constants.[18]

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(17) Mukerjee, P.; Mysels, K. J. "Critical Micelle Concentrations of Aqueous Surfactant Systems"; National Bureau of Standards: Washington, D.C., 1971.

(18) Sepulveda, L. *J. Colloid Interface Sci.* **1974**, *46*, 372.

Conversion of Formaldehyde to Acetic Acid. Formic Acid as a Stoichiometric CO Substitute

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We recently reported[1] the reactions in eq 1 and 2. In the course of that work we found that the reaction of formaldehyde with 65% aqueous HI and 500 psi of CO at 100 °C results in its quantitative conversion to CH_3CO_2H.[2]

$$CO \xrightarrow{HI,\ H_2O} CH_3CO_2H \qquad (1)$$

$$CH_3CO_2H + CO \xrightarrow{HI,\ H_2O} CH_3CH_2CO_2H \qquad (2)$$

Since these are elementary transformations that involve simple organic molecules, we regard this chemistry as being basic. However, in this and in an extensive body of other chemistry of carbon monoxide, rather high pressures can be required. A variant of this chemistry that could be effected under ordinary laboratory conditions would therefore be quite useful.

The Koch–Haaf reaction[3] involves the use of HCO_2H, the hydrate of CO, in substantial excess as a substitute for

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