ple, reaction in aqueous OH^- is slowed by added *tert*-butyl alcohol,[18] and in 1-BuOH:H_2O (94:6) reaction is only slightly faster than that in water (Table II), whereas for reaction of 2,4-dinitrofluorobenzene the rate is increased by orders of magnitude.[7b] The organic solvents lower the free energy of the hydrophobic pNPDPP, and this rate-inhibiting effect offsets the rate-enhancing effect of increased nucleophilicity of OH^- with decreasing water content of the solvent.

Spectroscopic probes suggest that the polarity of the Stern layer of a normal micelle, or the surface of an o/w microemulsion droplet, is lower than that of water and similar to that of a primary alcohol.[5,6,11,12] There are considerable uncertainties involved in relating kinetic solvent effects with bulk solvent properties such as dielectric constant, or Z or E_t parameters, but the effects of organic solvents upon reaction of pNPDPP with OH^- suggest that the relatively low polarity of a micelle might slow this reaction but have little effect on reactions of OH^- with less hydrophobic substrates such as carboxylic esters or halonitrobenzenes. There is evidence that micellar second-order rate constants for reaction of pNPDPP with hydroxide or alkoxide ion are slightly smaller, relative to reaction in water, than those for reactions such as deacylation or aromatic nucleophilic substitution.[28,33] However, all these comparisons depend upon the assumed volume element of reaction and the location of reactants at the micelle–water interface. There is also the possibility of reaction of OH^- in water with substrate in the micelle, and there is evidence for such a reaction; cf. ref 28, 34, and 35.

Qualitatively, the comparisons of *overall* rate effects on reactions of pNPDPP in micelles or microemulsion droplets suggest that although the substrate binds effectively to the micelle or droplet, the rate enhancements are small, relative to those for aromatic nucleophilic substitution, for example,[5,7,33]

Acknowledgment. Support of this work by the U.S. Army Office of Research is gratefully acknowledged.

Registry No. 2, 20317-32-2; 3, 86088-75-7; pNPDPP, 10359-36-1; CTABr, 57-09-0; OH^-, 14280-30-9; *tert*-amyl alcohol, 75-85-4; octane, 111-65-9; benzyl alcohol, 100-51-6; 1-butanol, 71-36-3; water, 7732-18-5; *tert*-butyl alcohol, 75-65-0; hexane, 110-54-3; *p-tert*-butylphenol, 98-54-4; 1-butoxide ion, 26232-84-8; benzylbutoxide ion, 26397-37-5.

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Nucleophilic Aromatic Substitution in Microemulsions of a Hydroxyethyl Surfactant

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Reactions of 2,4-dinitrochloro- or 2,4-dinitrofluorobenzene in microemulsions of hexadecyl(2-hydroxyethyl)dimethylammonium bromide (1), *n*-octane, and *tert*-amyl alcohol or 1-butanol, and NaOH give an ether by attack of the alkoxide zwitterion of 1. This ether slowly reacts with OH^-, giving 2,4-dinitrophenoxide ion. These reactions are slower than those in aqueous micelles. A Meisenheimer complex is formed by reaction of 1-chloro-2,4-dinitronaphthalene in these microemulsions and in those containing 1-butanol, and it is slowly converted into the naphtholate ion by attack of OH^-.

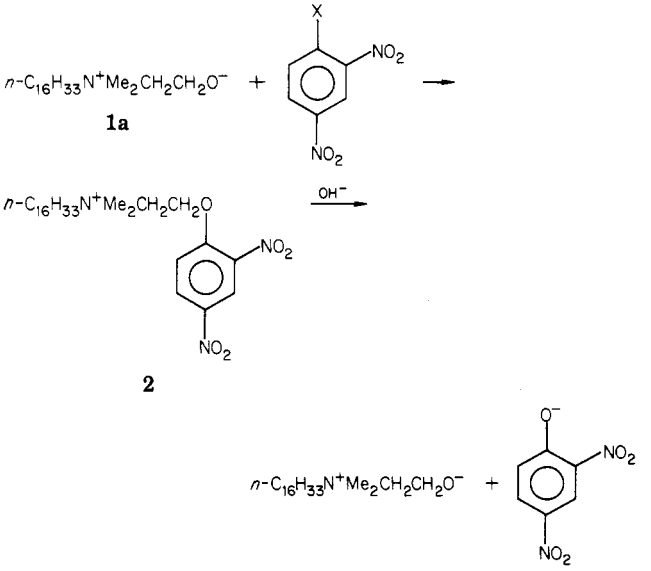
At high pH, an alcohol cosurfactant in a microemulsion can give an alkoxide ion that reacts nucleophilically in dephosphorylation[1] and in aromatic substitution on 2,4-dinitrohalobenzene.[2]

These reactions are mechanistically similar to dephosphorylation and aromatic nucleophilic substitution in micelles of hexadecyl(2-hydroxyethyl)dimethylammonium bromide (1) in which the alkoxide moiety of the zwitterion (**1a**) is the reagent and is much more reactive than OH^-.[2b,3]

$$\underset{\mathbf{1}}{n\text{-}C_{16}H_{33}N^+Me_2CH_2CH_2OH} + OH^- \rightleftarrows \underset{\mathbf{1a}}{n\text{-}C_{16}H_{33}N^+Me_2CH_2CH_2O^-}$$

Reactions of micellized **1** and **1a** with 2,4-dinitrohalobenzenes give an intermediate ether (**2**), which goes forward to 2,4-dinitrophenoxide ion (Scheme I), and both steps can be followed kinetically.[3b]

Scheme I[a]



[a] X = F, Cl.

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0022-3263/83/1948-2461$01.50/0

Table I. Reaction of DNCB in Microemulsions[a]

run	1 %	1 10^2x	alcohol[b] %	alcohol[b] 10^2x	octane, %	H_2O, %	$10^2[OH^-]$,[c] M	10^3k_ψ, s^{-1}	$k_\psi/[OH^-]$, $M^{-1}\ s^{-1}$
1	16.7	1.23	16.7	6.00	16.7	50.0	2.0	0.78	39
2	16.7	1.23	16.7	6.00	16.7	50.0	5.0	1.70	34
3	16.7	1.23	16.7	6.00	16.7	50.0	10.0	3.53	35
4	16.4	1.21	16.4	5.85	16.4	50.8	14.4	4.79	33
5	26.7	3.65	26.7	17.7	26.7	20.0	10.0	2.88	29
6	18.6	1.52	18.6	7.38	18.6	44.2	10.0	2.81	28
7	16.7	1.23	16.7[d]	7.07	16.7	50.0	4.0	0.70	18

[a] At 25.0 °C; x = mole fraction, % = percentage by weight. [b] *tert*-Amyl alcohol except where noted. [c] In moles per total volume of solution. [d] 1-Butanol.

Aromatic nucleophilic substitution is a very convenient reaction for this type of study because it is easy to distinguish spectrophotometrically between the products of reaction with alkoxide and hydroxide ion. As a result, one can obtain additional information regarding the reactive nucleophiles by examining nucleophilic substitution rather than dephosphorylation. The products of attack by alkoxide ion upon a phosphate ester have been identified qualitatively,[1,3c] but because one typically follows formation of a nitrophenoxide ion it is difficult to distinguish, quantitatively, between attack by hydroxide and alkoxide ion, as shown for reactions of *p*-nitrophenyl diphenyl phosphate:

$$(PhO)_2POOC_6H_4NO_2 \xrightarrow{OH^-} (PhO)_2PO_2^- + {}^-OC_6H_4NO_2$$

$$\xrightarrow{OR^-} (PhO)_2POOR + {}^-OC_6H_4NO_2$$

We examined these reactions of 2,4-dinitrochloro- and -fluorobenzene (DNCB and DNFB, respectively) in microemulsions of **1**, *n*-octane, and an alcohol cosurfactant, where an ether is the first-formed product. This ether (**2**) should bind very strongly to the microemulsion droplet and will decompose by attack of OH^- in the droplet. In most of the experiments the cosurfactant was *tert*-amyl alcohol to avoid reaction with alkoxide ion derived from cosurfactant. We also examined reactions of 2,4-dinitrochloronaphthalene (DNCN), which binds more strongly than DNCB and DNFB to droplets and micelles, and where reaction with **1a** gives an ether, which may then form a Meisenheimer complex.[4]

Experimental Section

Materials. Preparation and purification of the surfactants and substrates have been described.[3] 1-Butoxy-2,4-dinitronaphthalene was prepared from DNCN and 1-BuONa/1-BuOH in C_6H_6 under reflux for 3 h.[4] The product was recrystallized (EtOH–H_2O) and chromatographed ($SiO_2/CHCl_3$). It had mp 68–69 °C, whereas the literature value is 60–61 °C,[5] but it had the expected NMR and exact mass spectra. The other reagents were commercial samples, purified by standard methods, as necessary.

Kinetics. Reactions were followed spectrophotometrically at 25.0 °C, and the first-order rate constants, k_ψ, are in reciprocal seconds. We followed formation of the 2,4-dinitrophenoxide ion at 358 nm. Reactions of DNFB and DNCB, giving ether and 2,4-dinitrophenoxide ion, were followed at the isosbestic point, 318 nm. For reactions of DNCN we used 459 nm, the isosbestic point between the Meisenheimer complex and 2,4-dinitronaphtholate ion. Disappearance of Meisenheimer complex was followed at 500 nm, and appearance of naphtholate ion at 390 nm. Substrate concnentrations, in terms of total solution volume, were 6×10^{-6} M.

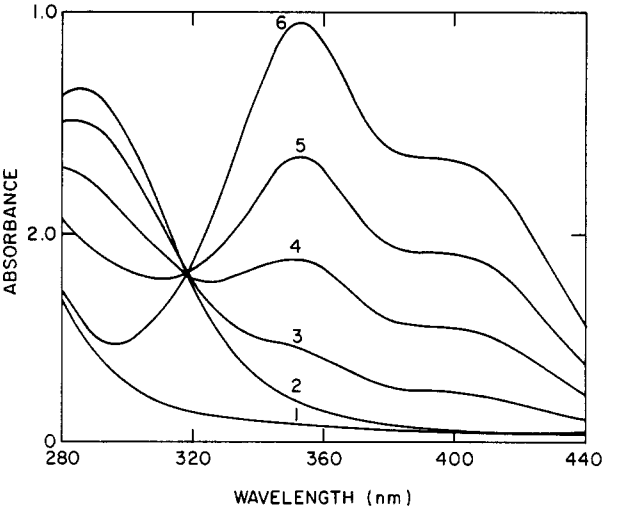

Figure 1. Repetitive spectral scans of a reaction mixture containing DNFB and 0.01 M NaOH, in equal amounts (w/w) of 1, *n*-octane, and *tert*-amyl alcohol and 50% H_2O: (1) no NaOH; (2) on addition of NaOH; (3–6) after 35, 105, 200, and 1110 min, respectively.

Products. The products of reactions of the aromatic substrates were identified by repetitive scanning of the reaction mixtures.[3b]

Results and Discussion

Reactions of 2,4-Dinitrohalobenzene. Repetitive spectral scans of the reaction mixtures show that ether **2** is first formed (λ_{max} 295 nm) and is converted into 2,4-dinitrophenoxide ion (λ_{max} 358 nm) (Scheme I). A typical scan for reaction of DNFB is shown in Figure 1, and 2,4-dinitrophenoxide ion is not formed directly. This behavior is similar to that in oil-in-water (o/w) microemulsions containing a primary alcohol cosurfactant at high pH[2] and in aqueous micelles of **1**.[3b]

The first-order rate constants for formation of ether from DNCB are listed in Table I. Reaction in a given microemulsion is first order with respect to $[OH^-]$. For a given $[OH^-]$, k_ψ is not very dependent on the composition of the microemulsion, although replacement of *tert*-amyl alcohol by 1-butanol slows the reaction, suggesting that there is no significant contribution of reaction with 1-butoxide ion. The hydroxyethyl surfactant (**1**), apparent $pK_a \simeq 12.4$ in a micelle,[3] is a stronger acid than 1-butanol,[6] so that **1a** should be the preponderant alkoxide species in a microemulsion droplet.

The first step of reaction of DNFB in microemulsions (Scheme I) is much faster than the second (Table II), and

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Table II. Reaction of DNFB in Microemulsions[a]

run	composition[b]	$10^2[OH^-]$,[c] M	10^3k_ψ, s^{-1}	$k_\psi/[OH^-]$, M^{-1} s^{-1}
1	A	0.10	34	34
2	A	0.50	174	35
3	A	0.80	277	35
4	A	1.00	343	34
5	B	4.00	0.064[d]	1.6×10^{-3}
6	B	7.00	0.116[d]	1.7×10^{-3}
7	B	10.0	0.164[d]	1.6×10^{-3}
8	C	0.50	120	24

[a] At 25.0 °C. [b] Equal amounts by weight of 1, *n*-octane, and alcohol: (A) 50.1 wt % H_2O, *tert*-amyl alcohol; (B) 50.8 wt % H_2O, *tert*-amyl alcohol; (C) 50.0 wt % H_2O, 1-butanol. [c] In terms of total volume of solution. [d] Conversion of ether 2 into 2,4-dinitrophenoxide ion.

we also examined the slower second step of decomposition of the intermediate ether **2**.[3b] As with DNCB, the initial reaction is first order with respect to $[OH^-]$ and the first step is also slightly slowed when *tert*-amyl alcohol is replaced by 1-butanol.

Decomposition of Intermediate Ether 2. Conversion of ether **2** into 2,4-dinitrophenoxide ion (Scheme I) in microemulsions is first order with respect to $[OH^-]$ (Table II), as expected, because OH^- is directly involved in the reaction. The reaction in the microemulsion is much slower than in aqueous micelles of **1**, where in 0.01 M OH^-, $k_\psi \simeq 0.2$ s^{-1} [3b] (these rate constants in micellar solutions go through maxima with increasing [1]). This rate difference, by a factor of ca. 60, suggests that the concentration, or reactivity, of OH^- in a microemulsion droplet is much lower than that in an otherwise similar micelle.[1,2a] However, the rate difference cannot be explained solely in these terms, because the chemically similar reactions of DNFB and DNCB with OH^- in microemulsions of *tert*-amyl alcohol are slower than those in aqueous micelles of CTABr by less than 1 order of magnitude.[2a] The differences may be related to the hydrophobicities of the ether (**2**) and the halobenzenes, DNFB or DNCB. The ether, with its hydrophobic alkyl group, may be located, on the average, more deeply in the microemulsion droplet than are the halobenzenes and therefore be less exposed to OH^-.

Although differences in the microemulsion compositions complicate comparisons, reaction of ether (**2**) in microemulsions of **1** (Table II) is faster than that of the 1-butyl ether in microemulsions containing 1-butanol.[2a,7] There should be no major differences in the concentrations of OH^- in the two sets of microemulsion droplets, suggesting that **2** is more reactive than the 1-butyl ether; cf. ref 3b and 8.

Formation and Decomposition of Meisenheimer Complexes. Reactions of 2,4-dinitrochloronaphthalene (DNCN) were examined in microemulsions of CTABr and *n*-octane, with either 1-butanol or *tert*-amyl alcohol as cosurfactant, and of **1** and *n*-octane, with *tert*-amyl alcohol as cosurfactant. The presence of alkoxide ion from either 1-butanol or **1** is responsible for formation of Meisenheimer complex, even though water is the bulk solvent.

Reaction in CTABr–*tert*-amyl alcohol microemulsions containing 10^{-2} M NaOH gave only the naphtholate ion, because OH^- is the reactive nucleophile,[9] but in the other systems either 1-butoxide ion or **1a** could be the nucleophile, and extensive amounts of Meisenheimer complex

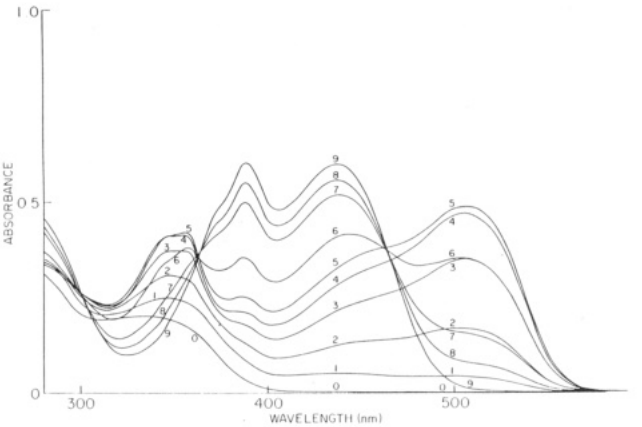


Figure 2. Repetitive spectral scans of a reaction mixture containing DNCN, 0.01 M NaOH, and a microemulsion of CTABr (5% w/w), *n*-octane (5% w/w), and butanol (10% w/w); (0) no NaOH; (1) on addition of NaOH; (2–9) after 0.2, 0.5, 1, 1.8, 2.5, 17.5, 26.3, and 42.3 h, respectively.

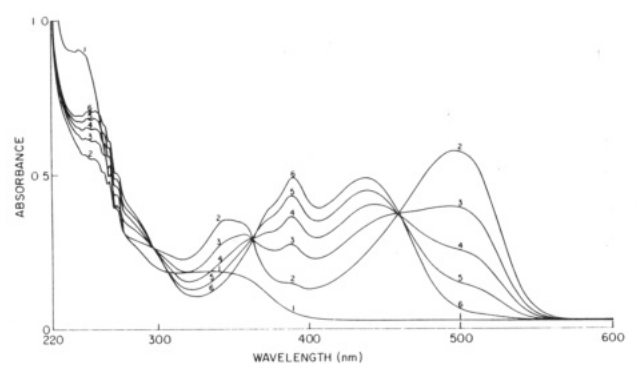


Figure 3. Repetitive spectral scans of a reaction mixture containing DNCN, 0.04 M NaOH, and a microemulsion of **1**, *n*-octane, and *tert*-amyl alcohol (Table III): (1) no NaOH; (2) on addition of NaOH; (3–6) after 5, 20, 40, and 80 min, respectively.

are formed. The results of a repetitive spectral scan of the reaction mixture are shown in Figure 2 for a 1-butanol microemulsion. Similar spectral scans were observed for reaction in the absence of surfactant in 1-butanol containing 6 wt % H_2O and 10^{-2} M NaOH, but an otherwise similar experiment in H_2O containing 5.8 wt % 1-butanol in water gave no evidence for formation of Meisenheimer complex, thus the microemulsion is akin to a medium of relatively high alcohol content.

A Meisenheimer complex is also formed in the reaction in a microemulsion containing **1** and *tert*-amyl alcohol (Figure 3). Its formation is relatively rapid, and it is converted into the naphtholate ion, presumably via the ether (Table III). There is an isosbestic point at 459 nm between the Meisenheimer complex and the naphtholate ion.

(7) In a microemulsion similar to those in runs 5–7 (Table II), $k_\psi/[OH^-]$ for reaction of 1-butoxy-2,4-dinitronaphthalene is ca 3×10^{-4} M^{-1} s^{-1}.

(8) Bunnett, J. F. *Q. Rev. Chem. Soc.* **1958**, *12*, 1. Miller, J. "Aromatic Nucleophilic Substitution"; Elsevier: New York, 1968.

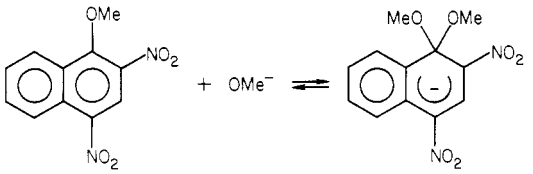
(9) Alkoxide ions generated from tertiary alcohols are much less nucleophilic than those from primary alcohols.[6a]

Table III. Reaction of DNCN in Microemulsions[a]

run	10^2[OH$^-$], M[b]	λ, nm	$10^3 k_\psi$, s^{-1}[c]	k_ψ/[OH$^-$], M^{-1} s^{-1}
1	1.0	465	5.5	0.55
2	4.0	459	25.5	0.64
3	8.0	459	49.2	0.62
4	12.0	459	70.4	0.59
5	15.0	459	86.9	0.58
6[d]	4.0	459	22.8	0.57
7	8.0	500	0.79	
8	12.0	500	0.84	
9	15.0	500	0.97	
10[e]	5.0	390	0.60	

[a] Composition (except where noted): 16.6% 1, 16.6% *tert*-amyl alcohol, 16.6% *n*-octane, and 50.2% H_2O (by weight). [b] In moles per total volume of solution. [c] At 25.0 °C. [d] 0.4% NaBr. [e] CTABr instead of 1.

The Meisenheimer complexes have λ_{max} at 505 nm (Figures 2 and 3), and their spectra are very similar to that of the methoxy Meisenheimer complex (**3**), for which the equilibrium constant is 240 M^{-1} in MeOH.[4,10]



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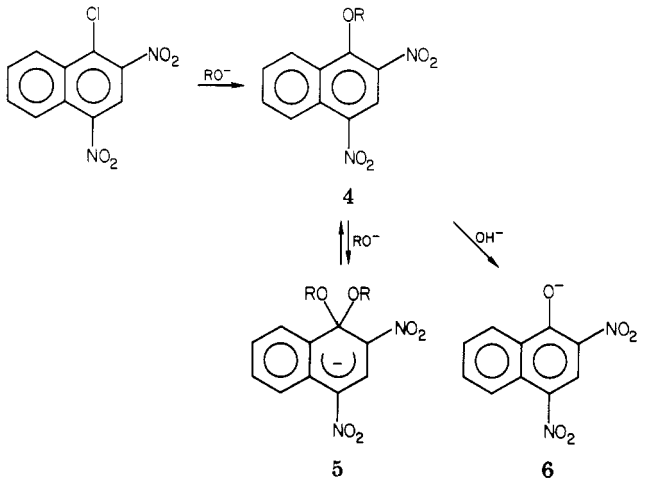
The reaction of DNCN in a microemulsion containing CTABr (5.0 % w/w), *n*-octane (5.0 % w/w), 1-BuOH (10.0 % w/w), and 10^{-2} M OH$^-$ (in terms of total solution volume) was followed at 463 nm (the isosbestic point of the complex and the naphtholate ion, Figure 2). Only the last part of the reaction was first order, with $k_\psi = 7.2 \times 10^{-4}$ s^{-1}. There was an induction period that was almost certainly due to buildup of the 1-butyl ether (**4a**), and for its directly followed conversion into Meisenheimer complex **5a**, $k_\psi = 7.7 \times 10^{-4}$ s^{-1}, under the same conditions. Equilibrium between the ether and Meisenheimer complex should be in favor of the latter,[4] so these observed first-order rate constants are close to that for conversion of ether **4a** into the Meisenheimer complex. (This reaction in the microemulsion is slower than that for reaction of methoxy ether with MeO$^-$ in MeOH,[4] where, in 0.01 M MeO$^-$, $k_\psi \simeq 9 \times 10^{-3}$ s^{-1}.) This difference suggests that the concentration of alkoxide ion in the microemulsion droplet is relatively low.

It was difficult to select a wavelength at which conversion of DNCN into 1-butyl ether **4a** could be followed (Figure 3), but the reaction followed at 290 nm was reasonably first order, with $k_\psi \simeq 3 \times 10^{-3}$ s^{-1}, which we assume to be the rate constant for disappearance of DNCN. This reaction is not much faster than conversion of ether **4a** into Meisenheimer complex **5a**. The probable overall reactions are shown in Scheme II.

There are obvious differences beween the reactions of DNCN in 1-butanol microemulsions and those containing the functional surfactant **1**. For example, there is no induction period for reactions in microemulsions of **1**, followed at the isosbestic point of 459 nm (Figure 3), suggesting that ether **4b** is formed rapidly from DNCN. The functional surfactant **1** is a stronger acid than 1-butanol,[3,6] and the greater concentration of **1a**, as compared with

(10) The structure of **3** was confirmed by its NMR spectrum.[4]

Scheme II[a]



[a] a, R = 1-Bu. b, R = $CH_2CH_2N^+Me_2C_{16}H_{33}$-*n*.

1-BuO$^-$, should make conversion of DNCN into ether **4b** relatively fast in microemulsions of **1**. Therefore, the reaction followed at 459 nm, or 465 nm for one experiment (Table III) should be the conversion of ether **4b** into the Meisenheimer complex (Scheme II). This reaction is first order with respect to [OH$^-$] and is not inhibited by NaBr (Table III, runs 1–6). Both these observations are consistent with the binding of anions to microemulsion droplets being weaker than binding to cationic micelles.

The relatively slow disappearance of the Meisenheimer complex, followed at 500 nm, involves formation of 2,4-dinitronaphtholate ion (Figure 3). This reaction is not very dependent upon [OH$^-$] (Table III, runs 7–9), as found in other systems.[4] The rate-limiting step involves attack of OH$^-$ upon ether **4b**, which is in equilibrium with the anionic Meisenheimer complex (Scheme II).

Reaction of OH$^-$ with DNCN (run 10) in microemulsions containing CTABr, rather than **1**, is relatively slow (Table III, run 10), which is consistent with reactivities of OH$^-$ and **1a** in cationic micelles.[3b]

Comparison with Reaction in Aqueous Micelles. Aromatic substitution on the halobenzenes by **1a** appears to follow the same reaction paths in microemulsions as in aqueous micelles (Scheme I). However, there are differences; for example, reactions in aqueous micelles are less than first order with respect to [OH$^-$], suggesting that there is extensive deprotonation of **1** in moderately concentrated OH$^-$, e.g., 0.01–0.1 M[3]. The first-order dependence of rate constants in microemulsions upon [OH$^-$] (Tables I, II, and III) shows that there is little deprotonation of **1** in these systems. We see the same kinetic form for dephosphorylation in microemulsions containing **1**, where reaction is first order in OH$^-$[2b] but less than first order in OH$^-$ micelles of **1**.[3a] This difference suggests that the concentration of OH$^-$ in the microemulsion droplets is considerably lower than that in cationic micelles of **1**. At least two factors could be at work: (i) the presence of alcohol cosurfactant in the microemulsion droplet reduces the charge density at the surface of the droplet and therefore its ability to bind OH$^-$ and (ii) the anions, e.g., OH$^-$, in the droplet are distributed over a larger phase volume in the microemulsion droplets than in micelles; cf. ref 1, 2, 11, and 12.

(11) Bunton, C. A.; de Buzzaccarini, F. *J. Phys. Chem.* **1982**, *86*, 5010.
(12) Mathews, W. K.; Larsen, J. W.; Pikal, M. J. *Tetrahedron Lett.* **1972**, 513. Zana, R.; Yiv, S.; Strazielle, C.; Lianos, P. *J. Colloid Interface Sci.* **1981**, *80*, 208.

Table IV. Reaction of DNCB in Different Systems[a]

system	product	$k_\psi/[OH^-]$, $M^{-1}\ s^{-1}$	k_{rel}
H_2O	2,4-dinitrophenoxide	1.4×10^{-4}	1
CTABr (micelles)	2,4-dinitrophenoxide	1.2×10^{-2} [b,c]	82
1 (micelles)	ether	2.0 [b,d]	14000
CTABr-*t*-AmOH (microemulsions)	2,4-dinitrophenoxide	1.6×10^{-3} [e]	11
CTABr-1-BuOH (microemulsions)	ether (major)	1.5×10^{-2} [e]	105
1-*t*-AmOH (microemulsions)	ether	3.5×10^{-2}	246

[a] In 0.01 M NaOH, 25.0 °C. [b] Maximum k_ψ. [c] In 0.01 M CTABr.[16] [d] In 0.005 M 1.[3b] [e] Reference 2.

Table V. Reaction of DNFB in Different Systems[a]

system	product	$k_\psi/[OH^-]$, $M^{-1}\ s^{-1}$	k_{rel}
H_2O	2,4-dinitrophenol	0.12	1
CTABr micelles	2,4-dinitrophenol	6.72 [b,c]	56
1 (micelles)	ether	720 [b,d]	6000
CTABr-*t*-AmOH (microemulsions)	2,4-dinitrophenol	0.7 [e]	6
CTABr-1-BuOH (microemulsions)	ether (major)	8 [e]	66
1-*t*-AmOH (microemulsions)	ether	35	292

[a] In 0.01 M NaOH, 25.0 °C. [b] Maximum k_ψ. [c] In 0.03 M CTABr.[16] [d] In 0.005 M 1.[3b] [e] Reference 2.

Rate enhancements are smaller in microemulsions than in aqueous micelles, as shown by values of $k_\psi/[OH^-]$ for reactions of DNCB and DNFB (Tables IV and V). These comparisons are however qualitative, because the micellar reactions are typically less than first order with respect to OH^-, and values of $k_\psi/[OH^-]$ go through maxima with increasing surfactant.[13-15] In addition, the halonitrobenzenes are not fully micellar bound in dilute surfactant,[16] but they should bind at the micelle–water interface, close to OH^-,[17] whereas they may spend some time in the apolar interior of an o/w microemulsion droplet. Qualitatively, the greater reactivity in systems in which alkoxide, rather than hydroxide, ion is the nucleophile is consistent with reactivities in the absence of surfactant.[3b,8] An additional point is that rate enhancements in functional and nonfunctional micelles and microemulsions are consistently larger for aromatic nucleophilic substitution than for dephosphorylation, regardless of substrate hydrophobicity.[2b,18]

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Registry No. 1, 20317-32-2; 1a, 54385-45-4; 2, 61095-52-1; OH^-, 14280-30-9; DNCB, 97-00-7; DNFB, 70-34-8; DNCN, 2401-85-6; CTABr, 57-09-0; 1-butanol, 71-36-3.

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Remarkably Selective Chlorination of Phthalic Anhydride and Its Monochlorinated Derivatives

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The vapor-phase chlorination of phthalic anhydride 1 and its monochlorinated derivatives 2 and 3 in the temperature range from 390 to 600 °C with elemental chlorine has been investigated and found to be highly selective. Thus, chlorination of 1 in the temperature range from 390 to 450 °C was found to give high yields of monochlorinated products accompanied by only small amounts of dichlorination with a high degree of regioselectivity favoring the formation of 4-chlorophthalic anhydride. Chlorination of a 3-chlorophthalic anhydride 3 by this method has provided the first direct synthesis of 3,5-dichlorophthalic anhydride 7 from phthalic anhydride via chlorination.

Electrophilic substitution reactions of phthalic anhydride 1 have received considerable attention over the years, and the lack of regioselectivity exhibited by these reactions is well-known. The nitration of phthalic anhydride under typical electrophilic substitution conditions gives rise to a nearly equal mixture of 3-nitro- and 4-nitrophthalic anhydrides.[1] Recently Zweig and Epstein have reported[2] that the Lewis acid catalyzed chlorination of phthalic anhydride in the molten state yields a mixture of monochlorinated isomers exhibiting regioselectivity similar to that observed in the nitration of phthalic anhydride and that polychlorination is a significant competing reaction. These workers also reported the detailed product isomer distribution of dichlorinated products obtained in the chlorination of phthalic anhydride and have rationalized their results in terms of the ortho- and para-directing effect of a chlorine substituent consistent with electrophilic substitution reactions. It has also been reported that the thermal and photochemical vapor-phase halogenation of monosubstituted benzene derivatives gives rise to rather unusual substitution patterns which differ markedly from those obtained in conventional electrophilic halogenations;[3,4] we were curious to see if the processes that lead

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