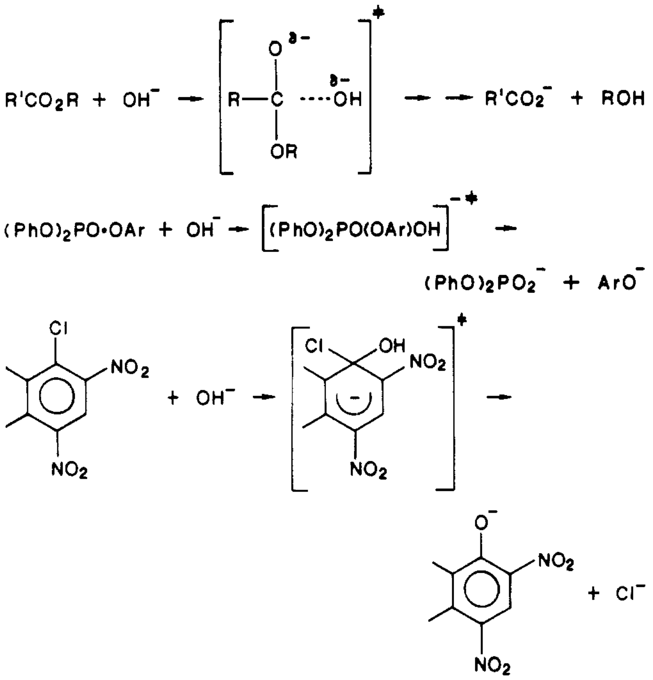
SCHEME I



lower than those in cationic micelles for reactions of OH^- with 2,4-dinitrochlorobenzene and 2,4-dinitrochloronaphthalene,[19,27] whereas the opposite sequence is formed for deacylation of *p*NPB and dephosphorylation of *p*-nitrophenyl diphenyl phosphate.

One possible cause of these different medium effects is that the substrates have different average locations in the micelles or droplets. For example, very hydrophobic substrates could be located deeply in the colloidal particles where they would be less accessible to hydrophilic anions. However, *p*NPB and 2,4-dinitrochloronaphthalene have similar micellar binding constants which does not support this hypothesis.[12,19]

Another explanation is that micelles, or other self-assembling colloids, have kinetic medium effects, related to mechanism and transition-state structure. For example, in anionic aromatic nucleophilic substitution the negative charge in the transition state is delocalized over a conjugated system and could interact readily with cationic head groups (Scheme I). In deacylation and dephosphorylation the charge in the anionic transition state is localized on oxygen atoms which will interact preferentially with water.[27,28]

This second explanation also seems to be applicable to reactions in normal aqueous micelles involving N_3^- as well as OH^-.[30]

This "solvent" effect of micelles or droplets is consistent with the rate decrease on addition of organic solvents to water (Figure 1). This inhibition is also observed for reaction of *p*-nitrophenyl diphenyl phosphate,[8] whereas addition of organic solvents speeds aromatic nucleophilic substitution by OH^-.[8] The transition states for deacylation and dephosphorylation should interact with hydrogen-bonding solvents such as water, and as water content is decreased destabilization of the transition state and stabilization of the apolar substrate opposes the rate-enhancing destabilization of hydroxide ion.

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Registry No. *p*NPB, 959-22-8.

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Reactions of Primary Amines with 2,4-Dinitrochlorobenzene in Microemulsions

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Reactions of 2,4-dinitrochlorobenzene with *n*-butyl-, *n*-amyl-, and *n*-hexylamine have been examined in microemulsions of *n*-octane and cetyltrimethylammonium bromide (CTABr) or sodium dodecyl sulfate (SDS) with amine as cosurfactant. The second-order rate constants in the microemulsion droplets are similar for reactions of *n*-butyl- and *n*-amylamine, but are lower for reaction with *n*-hexylamine, especially in the anionic microemulsions. With this exception second-order rate constants are similar to those in water.

Oil-in-water (o/w) microemulsions contain an oil, a surfactant, and a cosurfactant which is often a medium chain length alcohol, but can be a moderately hydrophobic molecule, and water is the bulk solvent.[1] Microemulsions are good solvents for ionic and nonionic solutes and their use as reaction media is well documented.[1b,2-4] They are similar to aqueous micelles in their ability to influence reaction rates. Overall rate effects are usually smaller in microemulsions, but their higher solubilizing power may be useful.

Bimolecular ionic reactions in microemulsions have been well studied, but effects on spontaneous reactions and reactions of nonionic nucleophiles have also been examined to a limited extent.[1b,2-6]

n-Hexylamine is a cosurfactant in microemulsions of cetyltrimethylammonium bromide (CTABr) and octane, and its reactivity toward 2,4-dinitrochlorobenzene (DNCB) in micro-

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TABLE I: Reaction in *n*-Alkylamine–Octane–CTABr Microemulsions[a]

R	H_2O, %	CTABr, %	RNH_2, %	octane, %	x_{RNH_2}/x_{CTABr}	$10^3 k_\psi$, s^{-1}	V_M', M^{-1}	$10^3 k_2'$, $M^{-1}\ s^{-1}$	V_M'', M^{-1}	$10^3 k_2''$, $M^{-1}\ s^{-1}$
Bu	50.0	11.5	33.1	5.40	14.4	20.8	0.39	1.8	0.45	2.1
Bu	54.0	10.6	30.4	5.00	14.4	17.6	0.36	1.5	0.41	1.7
Bu	57.9	9.64	27.8	4.66	14.4	15.9	0.33	1.4	0.37	1.6
Bu	62.8	8.59	24.7	3.91	14.4	15.9	0.29	1.4	0.33	1.5
Bu	54.0	8.18	32.8	5.02	20.0	19.7	0.37	1.6	0.41	1.8
Bu	54.0	6.94	34.8	4.26	25.0	19.4	0.38	1.6	0.42	1.7
Bu	54.0	6.08	36.6	3.32	30.0	23.6	0.39	1.8	0.43	2.0
Am	82.0	6.57	8.17	3.26	5.26	7.72	0.12	0.9	0.15	1.2
Am	81.7	5.43	9.79	3.08	7.56	8.70	0.13	1.0	0.15	1.2
Am	83.2	4.20	10.0	2.60	10.0	9.01	0.12	0.9	0.14	1.5
Am	81.2	3.69	12.8	2.31	14.7	10.6	0.15	1.1	0.17	1.2
Am	80.3	3.62	14.2	1.88	16.4	11.0	0.16	1.1	0.18	1.2
Am	80.5	3.07	14.6	1.83	19.9	11.5	0.16	1.1	0.18	1.2
Am	82.2	2.80	13.8	1.20	20.7	11.5	0.15	1.1	0.17	1.2
Am	80.9	2.47	15.4	1.23	26.2	11.7	0.17	1.1	0.18	1.2
Am	80.3	2.22	16.3	1.18	30.8	11.7	0.17	1.1	0.19	1.2
Am	78.5	2.00	18.2	1.30	38.1	11.5	0.19	1.1	0.20	1.0
Am	80.9	1.62	16.8	0.68	43.5	12.3	0.18	1.2	0.18	1.2
Am	80.2	1.21	17.5	1.09	60.3	12.1	0.18	1.1	0.19	1.1
Am	81.2	0.81	17.5	0.49	90.0	14.3	0.18	1.3	0.18	1.3
Am	68.8	8.97	15.5	6.73	7.24	11.1	0.20	1.3	0.25	1.5
Am	73.9	7.52	13.0	5.58	7.24	10.7	0.17	1.3	0.21	1.5
Am	77.7	6.42	11.1	4.78	7.24	9.70	0.14	1.1	0.18	1.4
Am	81.4	5.32	9.20	4.08	7.24	10.3	0.12	1.2	0.15	1.4
Am	85.5	4.17	7.20	3.13	7.24	9.23	0.09	1.0	0.11	1.2
Hx	85.6	11.48	1.60	1.32	0.51	1.29	0.074	0.6	0.13	1.1
Hx	86.2	9.82	2.34	1.64	0.86	1.93	0.073	0.6	0.12	1.0
Hx	84.7	9.81	3.38	2.11	1.25	2.33	0.083	0.6	0.13	0.9
Hx	85.0	8.88	4.22	1.90	1.72	2.65	0.087	0.5	0.13	0.8

[a] At 25.0 °C; percentage by weight.

emulsions has been compared with that in the absence of surfactant.[6]

In the present work we compare reactivities of *n*-butyl-, *n*-amyl-, and *n*-hexylamine as nucleophiles in microemulsions. The surfactants were CTABr or sodium dodecyl sulfate (SDS) so we compared the effects of charge of the microemulsion droplets and of the alkyl group of the amine. We also extended the concentration range of *n*-hexylamine used in the earlier work.

The rate constants for reaction of *n*-hexylamine with DNCB in cationic microemulsions were analyzed to estimate second-order rate constants in the microemulsion droplets.[6] One of the aims of the present work was to test this treatment on reactions of less hydrophobic amines than *n*-hexylamine.

Experimental Section

Materials. Surfactants were purified by recrystallization from Et_2O–EtOH (CTABr) or by repeated recrystallizations from H_2O followed by washing with Et_2O.[4,5] There were no minima in plots of surface tension against log concentration. The amines were redistilled, and DNCB was recrystallized (EtOH). The microemulsions formed spontaneously and the clear solutions showed no tendency to phase separate at 25 °C.

Kinetics. Rections were followed spectrophotometrically at 345 nm with Gilford or Beckman spectrophotometers. The substrate was added in MeCN and the reaction solution contained 3×10^{-5} M DNCB and 0.05% MeCN. First-order rate constants, k_ψ, s^{-1} were measured at 25.0 °C by using a simple linear first-order program or one based on Guggenheim's method.

Results and Discussion

n-Hexylamine is only sparingly soluble in water, but reaction of DNCB with *n*-butylamine has been followed, without surfactant or added solvent, and at 25.0 °C the second-order rate constant, $k_W = 0.84 \times 10^{-3}$ $M^{-1}\ s^{-1}$ from results with dilute amine.[6] In *t*-BuOH/H_2O 3:2 (w/w) the second-order rate constant is 1.43×10^{-3} $M^{-1}\ s^{-1}$ at 25.0 °C.

First-order rate constants for reactions of *n*-butyl-, *n*-amyl-, and *n*-hexylamine in cationic microemulsions are in Table I. The rate constants for reactions in anionic microemulsions of SDS are in Table II.

Qualitatively reactions are slightly faster in cationic than in anionic microemulsions and rates decrease with increasing length of the alkyl group of the amine, based on values of $k_\psi/[RNH_2]$ where amine concentration is written in terms of total solution volume. They also decrease with a decreasing ratio of amine to surfactant or increasing water content of the solvent.

These correlations between rate and composition of the microemulsion may be misleading, because we could obtain only low concentrations of *n*-hexylamine, especially with microemulsions based on SDS, whereas mole ratios of amine to surfactant were much larger in the other systems.

The effects of micelles and similar self-assembling colloids upon the rates of bimolecular reactions can be analyzed quantitatively by estimating the concentrations of both reactants in the colloidal particles, which are treated as a distinct reaction medium, i.e., as a pseudophase.[7-9] This general treatment has been applied to microemulsions and various approximations have been used in estimating the concentration of a nucleophile, for example, in the droplets.[1b,2,4-6]

Mole ratios of ionic reagents to surfactant head groups often correlate with rate constants of reactions in aqueous micelles.[7,8b] However, rate constants of the amine reactions do not follow the mole ratios of amine to surfactant in the microemulsions, except for the reaction of *n*-hexylamine in anionic microemulsions. This correlation may be fortuitous because only a limited range of amine could be examined (Tables I and II).

Another approach is to relate rate constant to mole fraction of amine, x_{RNH_2}, i.e., to $[RNH_2]/([RNH_2] + [CTABr])$ or $[RNH_2]/(RNH_2] + [SDS])$, which should approximately give the coverage of the droplet surface by amine. This correlation

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TABLE II: Reaction in *n*-Alkylamine–Octane–SDS Microemulsions[a]

R	H_2O, %	SDS, %	RNH_2, %	octane, %	x_{RNH_2}/x_{SDS}	10^3k_ψ, s^{-1}	V_M', M^{-1}	$10^3k_2'$, M^{-1} s^{-1}	V_M'', M^{-1}	$10^3k_2''$, M^{-1} s^{-1}
Bu	60.1	8.00	27.9	4.00	13.8	15.5	0.32	1.3	0.36	1.5
Bu	65.0	7.00	24.4	3.60	13.8	13.7	0.28	1.1	0.31	1.3
Bu	70.0	6.00	21.0	3.00	13.8	11.5	0.24	0.96	0.27	1.1
Bu	75.0	5.00	17.5	2.50	13.8	10.0	0.20	0.84	0.22	0.92
Bu	70.3	7.60	19.2	2.90	9.99	8.6	0.23	0.75	0.27	0.88
Bu	70.0	5.10	23.1	1.80	18.0	11.3	0.26	0.93	0.28	1.0
Bu	69.6	3.80	24.3	2.30	25.1	12.2	0.26	0.96	0.28	1.0
Bu	70.0	3.30	24.8	1.90	30.0	12.9	0.26	0.99	0.28	1.1
Am	74.4	6.40	12.8	6.40	6.61	6.54	0.16	0.71	0.19	0.84
Am	81.2	4.70	9.40	4.70	6.61	5.80	0.12	0.64	0.14	0.75
Am	84.1	3.98	7.95	3.97	6.61	5.45	0.099	0.59	0.12	0.72
Am	88.6	2.85	5.70	2.85	6.61	4.65	0.071	0.51	0.085	0.61
Am	86.3	2.66	9.14	1.90	11.4	6.83	0.11	0.68	0.12	0.78
Am	82.0	2.66	12.5	2.84	15.5	8.98	0.14	0.88	0.15	0.94
Am	81.9	2.50	13.3	2.30	17.6	9.65	0.15	0.92	0.16	1.1
Am	81.1	2.17	14.5	2.23	22.1	11.1	0.16	1.1	0.17	1.1
Am	81.5	1.59	15.3	1.61	31.9	11.6	0.16	1.1	0.17	1.1
Am	80.0	1.40	17.1	1.50	40.3	11.9	0.18	1.1	0.19	1.1
Am	80.0	1.14	17.7	1.16	51.4	13.3	0.18	1.2	0.19	1.2
Am	80.3	0.97	17.8	0.93	61.0	12.3	0.18	1.1	0.19	1.1
Am	81.7	0.68	16.9	0.72	82.3	12.5	0.17	1.1	0.18	1.2
Hx	85.1	10.6	2.39	1.91	0.64	0.45	0.077	0.15	0.13	0.20
Hx	83.1	10.7	2.54	3.66	0.68	0.56	0.079	0.18	0.13	0.30
Hx	87.2	8.62	2.12	2.06	0.70	0.53	0.064	0.16	0.11	0.27
Hx	88.7	7.05	1.96	2.29	0.79	0.59	0.055	0.17	0.09	0.28
Hx	83.8	10.0	2.96	3.24	0.84	0.71	0.080	0.20	0.13	0.32
Hx	87.4	7.84	2.39	2.37	0.87	0.70	0.063	0.19	0.10	0.30
Hx	82.3	10.6	3.27	3.83	0.88	0.73	0.085	0.19	0.14	0.32
Hx	84.3	9.55	2.96	3.19	0.89	0.77	0.077	0.20	0.13	0.33
Hx	85.5	8.85	2.82	2.83	0.91	0.76	0.073	0.20	0.12	0.32
Hx	89.0	6.49	2.12	2.39	0.93	0.71	0.054	0.18	0.086	0.29
Hx	81.9	10.9	3.63	3.57	0.95	0.76	0.090	0.19	0.15	0.31
Hx	84.0	9.46	3.21	3.33	0.97	0.84	0.079	0.21	0.13	0.33
Hx	83.4	9.60	3.37	3.63	1.00	0.90	0.082	0.22	0.13	0.35
Hx	87.5	7.33	2.62	2.55	1.00	0.81	0.063	0.20	0.10	0.31
Hx	82.3	9.08	3.32	5.30	1.00	0.79	0.079	0.19	0.12	0.30
Hx	83.7	9.48	3.56	3.26	1.10	0.86	0.083	0.20	0.13	0.32
Hx	80.3	7.42	3.15	9.13	1.20	0.95	0.069	0.21	0.11	0.32

[a] At 25.0 °C; percentage by weight.

is reasonably satisfactory for reactions of *n*-butyl- and *n*-amylamine. In cationic microemulsions $10^3k_\psi/x_{RNH_2}$ ranges from 17 to 24 and 9–13 s^{-1} for *n*-butyl- and *n*-amylamine, respectively, and in anionic microemulsions the corresponding ranges are 9–17 and 7–13 s^{-1} (Tables I and II). The correspondence is worse for *n*-hexylamine for which $10^3k_\psi/x_{RNH_2}$ ranges from 4 to 12 s^{-1} in cationic microemulsions, but is in the range 1–2 s^{-1} in anionic microemulsions, from data in Table I and II and ref 6. These differences cannot be due to incomplete binding of the amines in the droplets, because *n*-hexylamine should bind much more strongly thasn the other amines.

We therefore followed the approach used earlier in a quantitative treatment of the reaction of *n*-hexylamine with DNCB in cationic microemulsions.[6] We assume that both reactants are fully bound to the droplets because the amines are cosurfactants and DNCB binds readily to aqueous micelles which have less solubilizing power than microemulsions. In addition inhibition of reaction of 2,4-dinitrofluorobenzene with OH^- by anionic microemulsions is evidence of strong binding of aromatic substrates.[4a]

We estimate the volume in which reaction occurs in two ways. In one assumption the alkyl groups of CTABr penetrate the hydrocarbon core, and reaction occurs in a region which contains the amine and half the volume of the alkyl groups of the surfactant.[6,10] The volume of this region in 1 L of solution is V'.

In the second the volume, V'', is that of amine plus surfactant. The volume of octane is not taken into account because reaction should take place in the outer regions of the droplets, and octane should be deep in the interior.

The second-order rate constants in the droplet pseudophase are given by

$$k_2' = k_\psi V'/[RNH_2] \tag{1}$$

$$k_2'' = k_\psi V''/[RNH_2] \tag{2}$$

where $[RNH_2]$ is amine molarity based on total solution volume.

The two sets of rate constants and the parameters used in their calculation are in Tables I and II.

Values of k_2' or k_2'' are not very different from the second-order rate constant, $k_W = 0.84 \times 10^{-3}$ M^{-1} s^{-1} for reaction of *n*-butylamine in water.[6] This comparison suggests that reaction is occurring in a water-rich environment, which accords with rates of spontaneous reactions in oil-in-water microemulsions and estimates of polarities at the droplet surfaces.[1b,5]

The second-order rate constants, k_2' or k_2'' (Table I), in cationic microemulsions vary within a factor of ca. 3 for the three amines over a wide range of microemulsion composition in which there is a 60-fold difference in the mole ratio of amine to surfactant. The rate constants for reaction of *n*-hexylamine in Table I agree with values of $10^3k_2'$ of 0.9–1.4 M^{-1} s^{-1} and of $10^3k_2''$ of 1.0–1.9 M^{-1} s^{-1} calculated earlier.[6]

Reasonably good agreement was also found for values of k_2' and k_2'' for reactions of *n*-butyl and *n*-amylamine in anionic microemulsions (Table II). However, these rate constants are much lower for reaction of *n*-hexylamine.

For reactions in cationic microemulsions, values of k_2'' vary less than those of k_2', by factors of 2.6 and 3.7, respectively; i.e., we get a better fit to the model by taking the reaction volume as that of surfactant plus amine, but for reactions of *n*-butyl- and *n*-amylamine the variations of k_2' and k_2'' are similar (Table I). The situation is similar for reactions in the anionic microemulsions

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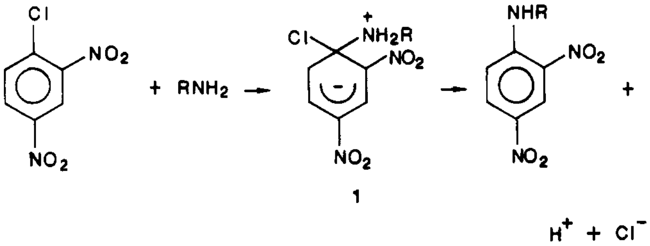
[10] In our calculations we assume unit density for all solutes, because the treatment is an approximate one and is not very sensitive to small changes in density.[6]

(Table II) except that if we include reaction of *n*-hexylamine the variations of k_2' and k_2'' are by factors of 8 and 7, respectively, whereas excluding *n*-hexylamine the variations are by factors of 2.2 and 2, respectively.

Values of k_2' or k_2'' in the droplets do not depend in any obvious way upon the alkyl group of the amine. This suggests that even *n*-butylamine is extensively bound to the droplets and that substrate and the three amines are located at the droplet surface in a water-rich region. Reaction of *n*-hexylamine in anionic microemulsions is an exception to this generalization because values of k_2' and k_2'' are considerably lower than those for the other reactions. This result suggests that the location of *n*-hexylamine in anionic microemulsion droplets is such that the amino group is not adjacent to the substrate which is polarizable and relatively hydrophilic and should be bound at the water-rich surface. However, the anionic microemulsions had a very low mole ratio of amine to SDS (Table II), which suggests that the low relative concentration of *n*-hexylamine may be causing the differences.

There appears to be a difference between reactivities in cationic and anionic droplets, which is relatively small except for reaction of *n*-hexylamine, based on values of k_2' or k_2'' (Tables I and II). The transition state for amine attack upon DNCB is probably similar to that of the Meisenheimer complex (**1**):[11]



Cationic head groups in a microemulsion could interact favorably with the delocalized negative charge on the aromatic residue in **1**, or the related transition state, and anionic head groups would interact unfavorably. There is evidence for these effects in micellar-mediated reactions.[12,13] However, these comparisons depend upon the assumptions made in calculating k_2' or k_2'', e.g., values of V' and V'' (eq 1 and 2) and the location and extent of binding of the reactants in the micellar droplets.

The pseudophase model, as initially developed for reactions in aqueous micelles, is reasonably satisfactory for reactions in o/w microemulsions,[1b,2–4] but there are some differences. Rate constants in micellar psesudophases can be related to reactant concentration in the micelle calculated as a mole ratio of reactant to micellized surfactant,[7,8b] but this approach fails for these amine reactions in microemulsion droplets. The properties of micellar surfaces probably do not change markedly with changes in concentration of counterionic reagents unless they are in high concentration and interact strongly with surfactant head groups.[7,14] The situation is different for microemulsions where the cosurfactant, which may also be the reagent, has a major role in stabilizing the droplet and may affect the surface as reaction medium.

Despite the wide variations in medium composition (Tables I and II) we do not see large variations in k_2' or k_2'' for a given amine or surfactant. These observations are consistent with the presence of discrete droplets whose surfaces are relatively unaffected by changes in medium composition.

There are not many bimolecular reactions of nionionic nucleophiles for which micellar effects have been analyzed quantitatively,[9a,12] but rate constants of these reactions in micellar pseudophases are not very much affected by hydrophobicity or concentration of the nucleophile or micellar charge. As with microemulsions, reactions seem to be slightly faster in cationic than in anionic micelles. However, these reactions in aqueous micelles have not been done with changes in concentration of the nonionic nucleophiles as large as those made in our microemulsion work, or with large changes in reagent hydrophobicities. Rates of the spontaneous hydrolysis of bis(4-nitrophenyl) carbonate are similar in aqueous micelles and in cationic microemulsions with alcohol cosurfactant, suggesting that water is available at the droplet surface.[5,15] The corresponding experiment has not been made with amine as cosurfactant, but we assume that water will also be present at the surfaces of these microemulsion droplets.

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Registry No. CTABr, 57-09-0; SDS, 151-21-3; 2,4-dinitrochlorobenzene, 97-00-7; butylamine, 109-73-9; amylamine, 110-58-7; hexylamine, 111-26-2; octane, 111-65-9.

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