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Catalytic Hydrolysis of Phosphate Esters in Microemulsions. 4. *p*-Nitrophenyl Diphenyl Phosphate Hydrolysis Catalyzed by Iodosobenzoate and Some of Its Derivatives

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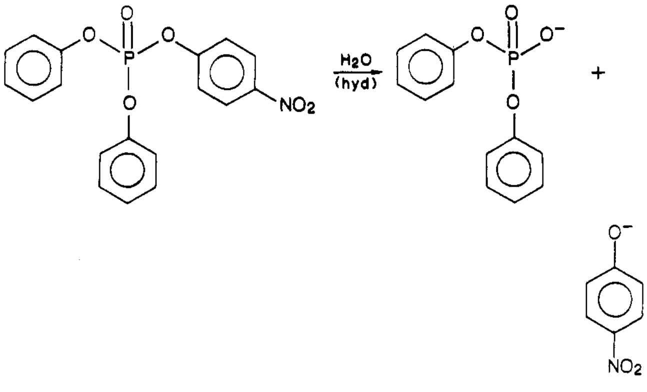
We have measured the second-order rate constants for the iodosobenzoate-catalyzed hydrolysis of *p*-nitrophenyl diphenyl phosphate in microemulsions of *n*-hexadecane and water stabilized by cetyltrimethylammonium chloride and three different cosurfactants: 1-butanol, *N*,*N*-dibutylformamide, and Adogen 464. In addition, we have compared the catalyst, iodosobenzoate, with four derivatives. Our results suggest that the predominant effect of these media on the hydrolysis reaction is electrostatic. Hence, we have extracted estimates of the surface potentials of the microemulsion droplets from rate constants.

Introduction

Several studies of the hydrolysis of phosphate esters have been reported over the period of the past 10 years.[1–4] Many of these investigations have involved organized media, either micellar solutions or microemulsions (μE). Recently, we reported the measurement of second-order rate constants for the hydrolysis of *p*-nitrophenyl diphenyl phosphate (PNDP), in cetyltrimethylammonium bromide (CTAB) microemulsions, both in the absence and presence of the catalyst iodosobenzoate (IBA). A comparison of the results of this work with the results obtained in CTAC micellar solutions shows that the reaction rate is much lower in the microemulsions.[5] On the other hand, the solubility of phosphate esters in the microemulsion is much higher than in the micellar solution (MS). These properties can be reconciled to some extent, in terms of the mechanism of the hydrolysis of PNDP and the differences between the structures of microemulsions and MS. It is assumed that the phosphate ester, being less polar, is more likely to be present in the oily interior of the microemulsion droplet, whereas the anionic IBA catalyst is likely to be predominantly in the more polar Stern layer and in the aqueous phase; these effects would reduce the opportunity for substrate–catalyst contact and result in higher solubility and lower reactivity in the microemulsion. In MS very little surfactant is present and, therefore, the MS does not offer high phosphate ester solubility, but the substrate is more vulnerable to attack by catalyst. The major goal of this study is to produce catalytic media that optimize the rate of phosphate ester hydrolysis in the presence of the OH⁻ and IBA-type catalysts for the reaction



where the rate is defined as

$$\text{rate} = k_{\text{hyd}} + k_{\text{IBA}}[\text{IBA}][\text{PNDP}] + k_{\text{OH}}[\text{OH}^-][\text{PNDP}] \quad (1)$$

k_{IBA} and k_{OH} are second-order rate constants.

In this paper are reported studies of the effects of different cosurfactants and of catalyst substituents on the rate of hydrolysis of phosphate esters in oil-in-water microemulsions stabilized with CTAB or CTAC.

Materials and Experimental Procedures

The sources of most chemicals, the discussion of experimental methods, the construction of microemulsion phase maps, and acquisition and analysis of rate data have previously been described.[5–7]

Cetyltrimethylammonium chloride was obtained from Eastman Kodak; a 29% aqueous solution was obtained from Akzo Chemie America under the trade name Arquad 16-29. Adogen 464, $(C_{8-10})_3N(CH_3)Cl$, 90% active material, and *N*,*N*-dibutylformamide, 99%, were purchased from Aldrich Chemical Co.

Results of Phase Map Studies

The phase map for the CTAB/1-BuOH microemulsion was previously reported by Hermansky and Mackay.[8,9] The ternary phase map representing the system composed of CTAC, Adogen 464, and 0.03 M aqueous borate buffer, denoted Aq, is shown in Figure 1. The different legends indicate mixtures which are clear (but exhibit the Tyndall effect), turbid, clear liquid crystalline, and turbid liquid crystalline. The mixtures with the percentages of CTAC or Adogen 464 each greater than 40% are very viscous, and significant regions of the map are turbid. On the basis of the composition of the optically clear regions of the ternary phase maps, pseudoternary phase map with emulsifier ratios (*E*) of 0.56, 0.79, 1.1, 2.3, 2.60, 3.88, and 5.08 CTAC to Adogen were produced and the first four are depicted in Figure 2. (In the name for a phase map (e.g., CTAC 0.56), the number indicates surfactant to cosurfactant mass ratio.)

CTAC 0.56 microemulsions are generally viscous at Aq mass percentages exceeding 50. CTAC 1.1 microemulsions are fluid, easy to prepare, and offer an appreciable region of clarity; many of the rate studies were conducted in these systems. A phase map

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TABLE I: Survey of Kinetics for Varying CTAC to Adogen 464 Ratios in Order of Decreasing Ratios[a]

entry	CTAC/Adogen	% CTAC	% Adogen	% aqueous	% hexadecane	pH	k_{IBA}, $(M{\cdot}s)^{-1}$
1	4.98	24.9	5.0	68.7	1.4	9.08	7.24
2	4.42	26.1	5.9	65.1	2.9	9.02	7.23
3	4.17	24.6	6.3	66.6	2.5	9.05	7.52
4	3.11	25.5	8.2	63.5	2.8	9.03	6.30
5	2.61	22.7	8.7	61.4	7.2	9.02	6.26
6	2.28	23.5	10.3	58.6	7.6	9.02	6.23
6 (low oil)	2.27	24.7	10.9	61.5	2.6	8.94	6.09
7	1.62	21.9	13.5	54.7	9.9	8.95	6.89
8	1.58	23.5	14.9	41.1	2.7	8.95	5.68
9	1.10	19.7	17.9	49.2	13.1	8.96	10.1
10	1.01	14.2	14.1	57.5	14.1	8.85	10.1
11	0.747	13.3	17.8	50.9	18.0	8.99	7.8
12	0.588	22.8	38.8	22.8	22.8	9.61	8.47
13	0.557	27.0	48.5	11.6	12.3	10	~13

[a] Range of [IBA] used: 2.49×10^{-4} to 0.194×10^{-4} M.

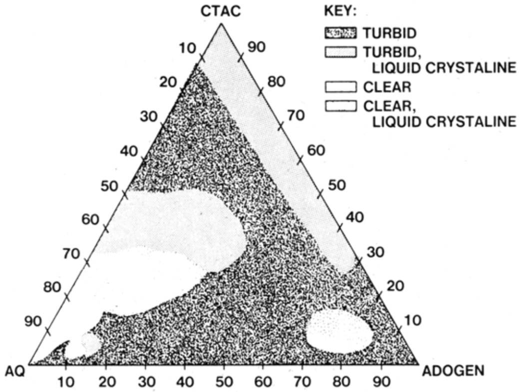

Figure 1. Ternary phase map for systems composed of CTAC, Adogen 464, and 0.03 M borate buffer.

representing the microemulsion called CTAC BuOH 1.1, which was prepared with 1-butanol as the cosurfactant, is depicted in Figure 3. The area of the clear region in CTAC BuOH 1.1 microemulsion is about twice the area found in CTAC 1.1. Butanol as a cosurfactant yields not only a much greater clear region but also forms less viscous microemulsions.

The ternary phase map representing the CTAC/*N,N*-dibutylformamide (DBF)/Aq system is shown in Figure 4. Pseudoternary phase maps with emulsifier mass ratios of 0.67, 1.0, and 1.5 CTAC to DBF are shown in Figure 5. The name for a phase map (e.g., CTAC DBF 0.67) again indicates a specific CTAC to DBF ratio. CTAC DBF 0.67 is more viscous than the other two CTAC DBF microemulsions; however, all three are good working fluids.

Results and Kinetics Studies

Effect of Cosurfactants. Rate constants were measured in CTAC/Adogen 464 stabilized microemulsion over a range of CTAC to Adogen 464 mass ratios from 0.557 to 4.98. The results are presented in Table I. The microemulsions become more viscous as the percent aqueous phase decreases. The k_{IBA} values lie predominantly between 6.25 and 8.50 $(M{\cdot}s)^{-1}$, however, the k_{IBA} values for entries 9 and 13 are much higher. The microemulsion corresponding to entry 9 has a surfactant to cosurfactant mass ratio of 1.1 CTAC to 1.0 Adogen 464, and will be known as CTAC 1.1. The microemulsion corresponding to entry 13 has a surfactant to cosurfactant mass ratio of 0.56 CTAC to 1.0 Adogen 464, and will be known as CTAC 0.56. Most of our kinetic studies were conducted in these media.

In order to contrast the cosurfactants Adogen 464 and 1-BuOH, hydrolysis studies were conducted in CTAC microemulsions in which 1-BuOH was used in place of Adogen 464. The results are tabulated in Table II where the entry numbers designate microemulsion compositions corresponding to those in Table I; e.g., the microemulsion corresponding to entry 3 in Table I contains 6.3% Adogen; entry 3 in Table II contains 6.3% 1-BuOH. The k_{IBA} values in the 1-BuOH system generally decrease with increasing percent 1-BuOH and are lower than the corresponding

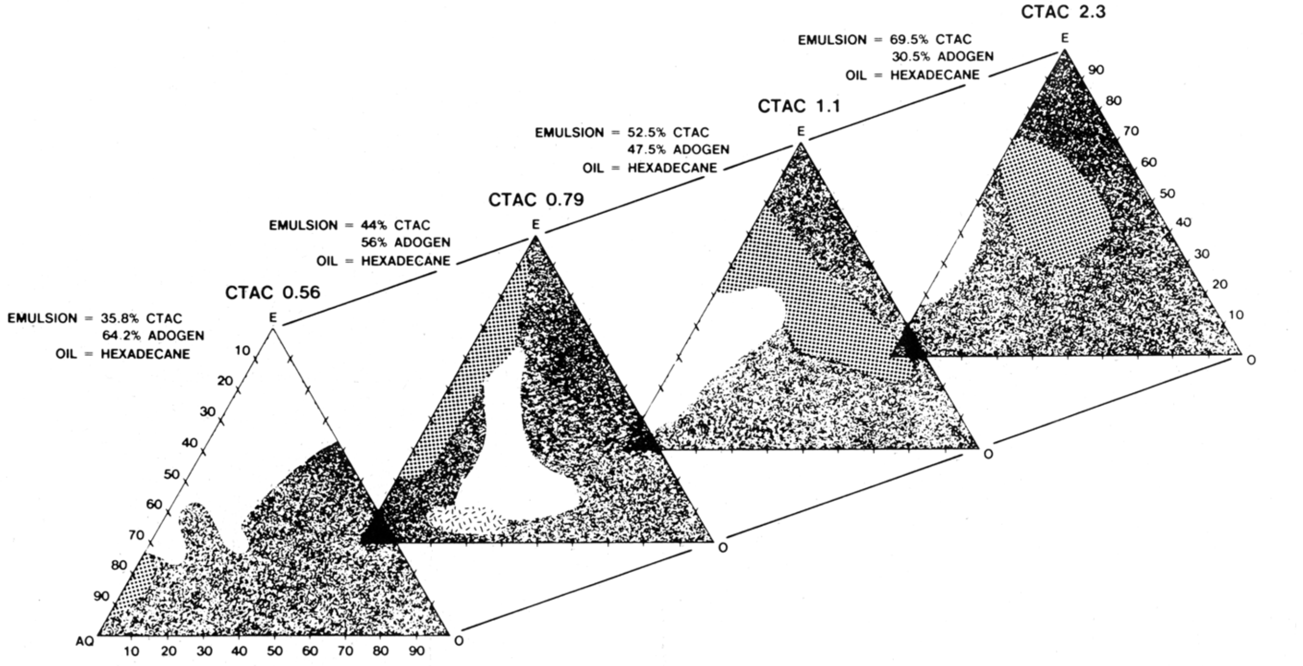

Figure 2. Pseudophase maps for systems composed of borate buffer, *n*-hexadecane, and fixed CTAC/Adogen 464 mass ratios. See Figure 1 for legend.

TABLE II: Survey of Kinetics for Varying CTAC to Butanol Ratios Matching Percentages Used for the CTAC/Adogen Microemulsion Formulations[a]

entry	CTAC/BuOH	% CTAC	% BuOH	% aqueous	% hexadecane	p*H*	k_{IBA}, $(M{\cdot}s)^{-1}$
1	4.98	24.9	5.0	68.7	1.4	9.00	4.43
3	4.17	24.6	6.3	66.6	2.5	9.16	5.41
5	2.61	22.7	8.7	61.4	7.2	8.87	4.30
6	2.28	23.5	10.3	58.6	7.6	9.10	2.71
9	1.10	19.7	17.9	49.2	13.1	9.38	1.16

[a] Percentages used for entries correspond to entry numbers cited in Table I.

TABLE III: Rate Constants in Systems Employing Combinations of the Cosurfactants Adogen 464 and Butanol

(a) CTAB/Cosurfactant Ratio 1.0; Range of [IBA] Used: 6.25×10^{-4} to 0.735×10^{-4} M; pH 9.3

% Adogen	% butanol	% CTAB	% aqueous	% hexadecane	k_{IBA}, $(M{\cdot}s)^{-1}$
4.48	13.4	17.9	59.7	4.48	0.221
8.95	8.95	17.9	59.7	4.48	2.54
13.4	4.48	17.9	59.7	4.48	tubrid fluid

(b) CTAC to Cosurfactant Ratio 1.1; Range [IBA] Used: 6.25×10^{-4} to 7.8 10^{-5} M; pH Range 9.01 to 9.19

% Adogen	% butanol	% CTAC	% aqueous	% hexadecane	k_{IBA}, $(M{\cdot}s)^{-1}$
5.96	11.9	19.7	49.3	13.1	3.07
8.90	8.90	19.7	49.3	13.1	3.99
11.9	5.96	19.7	49.3	13.1	5.42

(c) CTAC to Cosurfactant Ratio 0.56; Range [IBA] Used: 1.25×10^{-3} to 0.419×10^{-4} M; pH 10.15 and 8.55, Respectively

% Adogen	% butanol	% CTAC	% aqueous	% hexadecane	k_{IBA}, $(M{\cdot}s)^{-1}$
41.1	14.3	23.1	9.94	11.1	1.34
48.5	0.00	27.0	12.9	11.6	~14

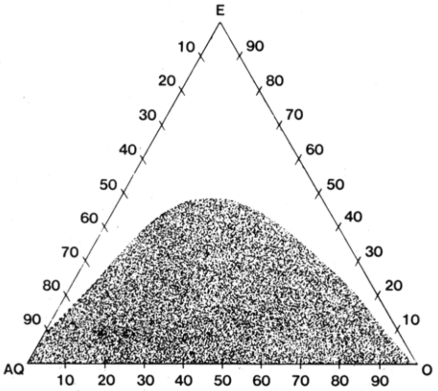

Figure 3. Pseudoternary map for systems composed of borate buffer, *n*-hexadecane, and a CTAC/1-butanol mass ratio of 1.1:1. See Figure 1 for legend.

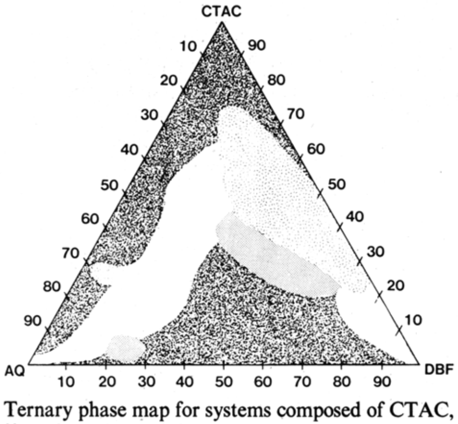

Figure 4. Ternary phase map for systems composed of CTAC, DBF, and borate buffer. See Figure 1 for legend.

TABLE IV: Variations in the Aqueous Phase in CTAC 0.56 Microemulsion[a]

% CTAC	% Adogen	% aqueous	% hexadecane	pH	k_{IBA}, $(M{\cdot}s)^{-1}$
27.0	48.5	11.6	12.9	10	14.0
25.8	46.3	17.6	10.3	8.42	5.69[b]
21.8	39.2	28.6	10.5	9.35	8.46
17.9	32.1	40.0	10.0	9.06	8.67

[a] Range of [IBA] used: 1.25×10^{-3} to 1.56×10^{-4} M. In order of increasing aqueous phase, with an uncertainty of ±10%. [b] Corrected k_{IBA} to include the % IBA not in the anionic form at pH 8.42.

Adogen 464 systems. In particular, the value of the rate constant for entry 9 is at least 9 times smaller than the corresponding Adogen 464 microemulsion. It should be noted that the butanol microemulsions are fluid and easier to work with than the majority of the Adogen 464 microemulsions.

Consideration of the kinetic advantage of Adogen and the fluidity conferred by 1-butanol suggests that a microemulsion composed of a combination of both cosurfactants be examined. Microemulsions with two different CTAC to combined-cosurfactant-mass ratios were prepared, corresponding to CTAC 1.1 and CTAC 0.56. In addition, a CTAB microemulsion with a surfactant to cosurfactant ratio of 1.0 CTAB to 1.0 cosurfactant was also used as a hydrolysis medium. The kinetic results, in order of decreasing percent butanol, are presented in Table III, along with the actual microemulsion compositions. In all three sets of experiments the k_{IBA} increases with decreasing percent butanol. Hence, the majority of the kinetic studies were conducted in the two CTAC/Adogen 464 microemulsions CTAC 1.1 and CTAC 0.56. The aqueous and oil phases were varied at constant surfactant to cosurfactant mass ratios in order to maximize the rate of hydrolysis.

Of all the media in which we have conducted phosphate ester hydrolysis studies the CTAC 0.56 system yields the highest values of k_{IBA} (Table IV). Unfortunately, this system is very viscous and difficult to bring to homogeneity. These results prompted experiments in which the percentage of aqueous phase was systematically varied. The results are presented in Table IV. Only when the aqueous phase approaches 40% by mass do fluidity and, hence, k_{IBA} reproducibility become acceptable.

The data presented in Table V indicate that the second-order rate constants in CTAC 1.1 are not as high as those measured in CTAC 0.56. However, the high buffer capacity, solubility, and the fluidity of the system permits a thorough kinetics investigation. With an increase in the percent aqueous phase, the k_{IBA} increases gradually until 89% aqueous borate buffer is reached, whereupon k_{IBA} rises dramatically to 20.3 (entry 8); this is reasonable, since this system approaches the condition of a micellar solution in this composition region. The rate data for the CTAC 1.1 systems again

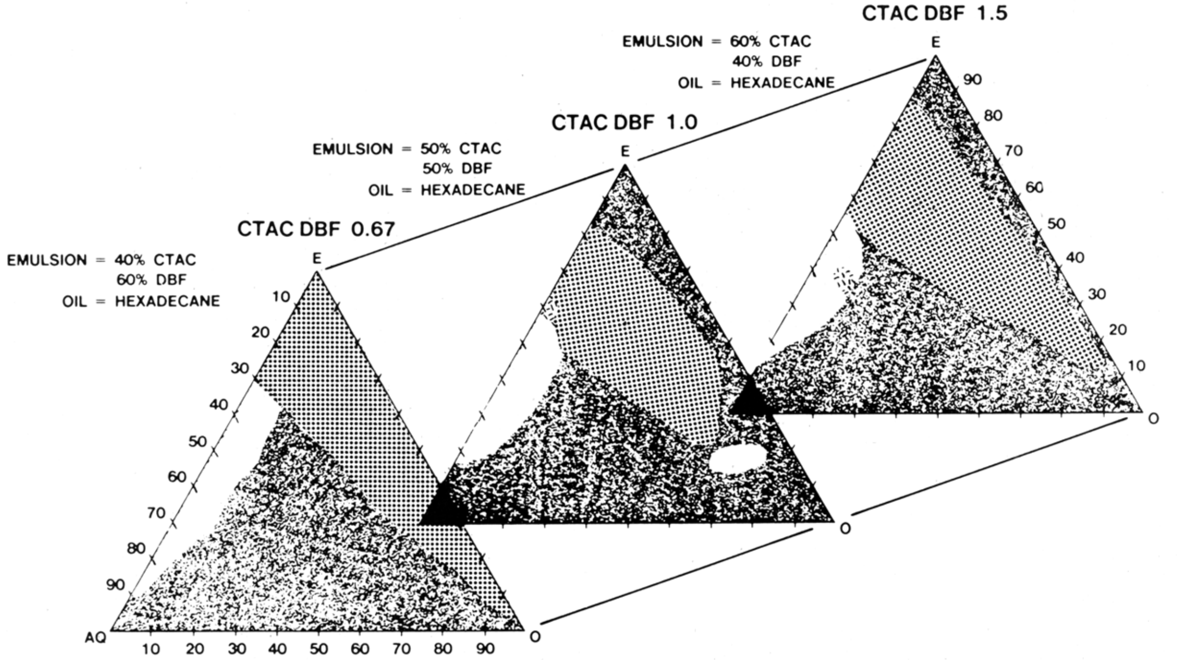

Figure 5. Summary of the pseudoternary phase maps for CTAC/DBF emulsifier mass ratios of 0.67, 1.0, and 1.5. See Figure 1 for legend.

TABLE V: Compositional Variations in CTAC 1.1 Microemulsions[a]

entry	pH	k_{IBA}, $(\mathrm{M{\cdot}s})^{-1}$	% emulsifier	% hexadecane	% aqueous
1	8.82	9.00	42.8	24.6	32.6
2	8.81	8.09	43.4	17.0	39.6
3[b]	9.11	8.92	34.4	20.4	45.1
4	9.05	8.68	37.6	13.1	49.2
5[b]	9.01	5.67	38.8	10.3	50.9
6	9.13	9.30	29.9	10.4	59.6
7	8.81	9.40	29.5	9.0	61.5
8[c]	9.13	20.3	9.7	1.1	89.2

[a] Range of [IBA] = $1.25 \times 0.156 \times 10^{-3}$ M. [b] Entries 3 and 5 have the same emulsifer to aqueous phase mass ratio. [c] [IBA] = $(0.156\text{–}0.078) \times 10^{-3}$.

TABLE VI: Survey of *N*,*N*-Dibutylformamide (DBF), as a Cosurfactant, in Order of Increasing Aqueous Phase

% CTAC	% DBF	% hexadecane	% aqueous	pH	k_{IBA}, $(\mathrm{M{\cdot}s})^{-1}$
(a) CTAC DBF 0.67					
21.8	32.7	9.1	36.4	7.84	2.94
12.5	18.8	5.9	62.7	8.65	3.919
7.8	11.6	3.0	77.6	8.77	5.105
(b) CTACDBF 1.0					
24.2	24.2	8.0	43.4	8.59	4.68
16.9	16.9	10	56.0	8.45	5.46
11.5	11.5	4.0	73.0	8.69	6.86
(c) CTAC DBF 1.5; Viscous					
28.2	18.8	5.9	47.0	8.80	6.23
22.0	14.7	8.1	55.0	8.76	6.23
16.9	11.2	6.3	66.0	8.67	7.16
(d) CTAC to Dibutylformamide Ratio: 1.0; No Oil Present					
26.3	26.3	0	47.5	8.70	4.51
17.5	17.5	0	65.0	8.64	5.59
7.5	7.5	0	85.0	8.80	10.2

can be summarized by the empirical equation: $k_{\mathrm{obsd}} = k_{\mathrm{hyd}} + k_{\mathrm{OH}}[\mathrm{OH}] + k_{\mathrm{IBA}}[\mathrm{IBA}]$; the uncertainty in the second-order constants, k_{OH} and k_{IBA}, is ~10%. In the most thoroughly studied CTAC 1.1 system (7, Table VI), the empirical equation is $k_{\mathrm{obsd}} = 0 + 0.55[\mathrm{OH}] + 9.4[\mathrm{IBA}]$.

The oil-in-water microemulsions stabilized by the surfactant CTAC and the cosurfactant DBF are colorless fluids of relatively low viscosity in comparison to the CTAC/Adogen 464 microemulsions. When the CTAC to DBF mass ratio approaches 1.5, the viscosity does increase. Microemulsions with three different CTAC to DBF mass ratios (0.67, 1.0, and 1.5) were examined and will subsequently be known as the CTAC DBF 0.67, CTAC DBF 1.0, and CTAC DBF 1.5 microemulsions. Table VI summarizes the data for the three different media, which are listed in order of increasing CTAC to DBF mass ratios, and within each ratio in the order of increasing percent Aq. A fourth medium containing no oil was also employed as a hydrolysis medium. All of the media show an increase in the k_{IBA} with respect to an increase in percent Aq, and an increase in the mass ratio of CTAC to DBF.

A comparison of the second-order rate constants obtained for microemulsions using DBF, Adogen 464, and 1-BuOH is shown in Table VII. The trends in the data show that k_{IBA} values are definitely affected by the nature of the cosurfactant; k_{IBA} values for Adogen systems are generally 2–3 times greater than in DBF systems and 4–5 times greater than in 1-butanol systems. This observation supports an older conclusion reached by Lindman[10–12] that alcohol actually breaks up the microemulsion structure. For the cosurfactants we have studied, the order of increasing effectiveness in the microemulsion medium for the hydrolysis of phosphate esters is 1-BuOH < DBF < Adogen 464.

IBA Derivatives. IBA and four of its derivatives were compared as catalysts in the CTAC 1.1 system with the composition of 15.5% CTAC, 14% Adogen 464, 9% hexadecane, and 61.5% aqueous. The results are summarized in Table VIII. The catalyst concentration range is indicated, the pH ranges from 8.77 to 9.12, and the results are listed in order of increasing electron-withdrawing character of the IBA substituent. Except in the cases of the *p*-nitro and the *o*-octoxy derivatives the k_{IBA} values decrease with increasing electron-withdrawing character of the IBA substituent as expected. The effect of the nitro group in PNIBA is unclear. Consideration of possible resonance structures does not aid in explaining the apparent increased rate constant. In this case, however, since $k_{\mathrm{PNIBA}} > k_{\mathrm{IBA}}$, the nucleophilicity of PNIBA seems greater than that of IBA; this implies that the *p*-nitro substituent somehow exhibits electron-donating character.

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TABLE VII: Compositions of CTAC DBF Microemulsions Compared to Similar Compositions of CTAC 0.56, CTAC 1.1, and CTAB Microemulsions

microemulsion	% CTAC	% cosurfactant	% hexadecane	% aqueous	k_{IBA}, (M·s)$^{-1}$
CTAC DBF 0.67	21.8	32.7	9.1	36.4	2.94
CTAC 0.56	17.9	32.1	10.0	40.0	8.67
CTAC DBF 1.0	24.2	24.2	8.0	43.4	4.68
CTAC 1.1	23.0	20.4	17.0	39.6	8.09
CTAC DBF1.0	16.9	16.9	10.0	56.0	5.46
CTAB	18.0	18.0	4.0	60.0	1.10

TABLE VIII: Comparison of IBA, IBA Derivatives, and IBX Catalysts in Microemulsions[a]

	k_{CAT}, (M·s)$^{-1}$	
[catalyst] × 10^3, M	CTAC 1.1	CTABμE
1.25–0.156 OIBA	6.52	1.40[6]
1.25–0.78 IBA	9.40	1.22[5]
0.625–0.078 NIBA	3.5	0.93[6]
1.25–0.156 CIBA	1.97	
0.193–0.024 PNIBA	11.42	
1.25–0.156 IBX	7.96	

[a] Systems for each microemulsion type used were CTAC1.1: 15.5% CTAC, 14.0% Adogen 464, 9.0% hexadecane, and 61.5% aqueous; CTABμE: 18.0% CTAB, 18.0% 1-butanol, 4.0% hexadecane, and 60.0% aqueous CTAC, 48.5% Adogen. OIBA, 5-octoxy-2-iodosobenzoic acid; IBA, 2-iodosobenzoic acid; NIBA; 5-nitro-2-iodosobenzoic acid; CIBA, 5-carboxy-2-iodosobenzoic acid; PNIBA, 4-nitro-2-iodosobenzoic acid; IBX, 4-methyl-2-iodoxybenzoic acid.

The second-order rate constant for OIBA should be higher than that for IBA. The octoxy substituent should increase the nucleophilicity at the I–O bond, and the C_8 tail should ensure that OIBA is deeper in the oil core and, therefore, closer to the substrate than IBA would be. Our experiments contradict this reasoning: we find $k_{IBA} > k_{OIBA}$.

One might expect to find, in analogy to the iodine–oxygen acids such as HIO_4, HIO_3, HIO_2, and HIO, that, as the number of O atoms bonded to iodine increases, the acidity increases and presumably the nucleophilicity decreases. This implies that k_{IBX} should be smaller than k_{IBA}. Our results show that k_{IBA} and k_{IBX} are virtually equal.

Discussion

In view of our work and many articles in the literature[13-15] it is clear that the predominant effect of organized media on the hydrolysis of phosphate esters is electrostatic: only cationic microemulsions afford appreciable catalysis and the studies reported here indicate that the second-order rate constant, k_{IBA}, is higher in the presence of a cationic cosurfactant. Taken together, we have a picture in which anionic IBA is attracted to the cationic head groups of the microdroplet whereupon it enters the Stern layer and is brought in contact with the substrate, which resides predominantly in the oil. Hence, the reaction rate constants appear to depend on conditions which affect the total charge or surface potential, Ψ, of the microdroplet.

Following the procedure of Mackay and Hermansky,[8] "phase volume corrected" rate constants were extracted from the data of this study and were used to estimate the surface potential of the microdroplets in three different microemulsion media relative to a nonionic Brij 96 microemulsion.

It is probable that the substrate, PNDP, resides predominantly in the oily interior of a microdroplet and that the anionic catalyst resides in the Stern layer and the aqueous region. Hence, the data collected in this study would be more significant if the concentrations of substrate and catalyst were recalculated in terms of "phase volume", ϕ, which is the volume fraction of the microemulsion occupied by surfactant, cosurfactant and oil; the quantity $1 - \phi$ is then the volume fraction of the aqueous phase. Making the phase volume corrections of the concentration we obtain

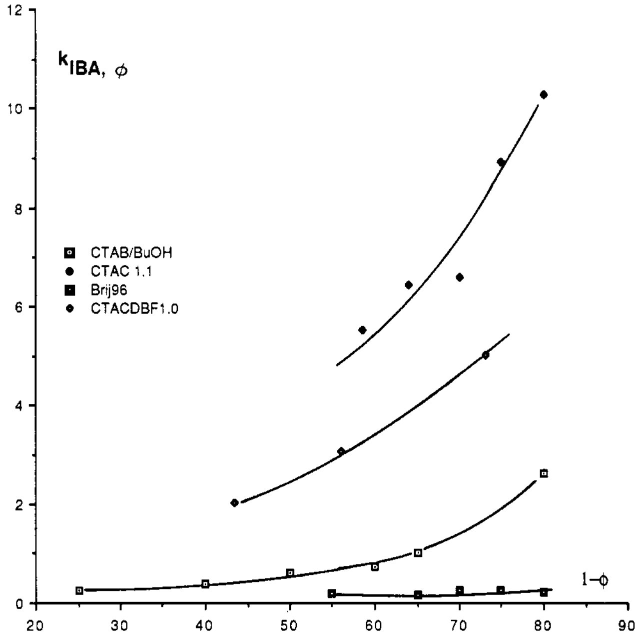

Figure 6. Plots of phase-corrected second-order rate constants vs the percentage aqueous volume.

$$d([PNDP]/\phi)/dt = (k_{IBA,\phi})([PNDP]/\phi([IBA]/(1 - \phi))) \quad (2)$$

where [PNDP] and [IBA] refer to bulk concentrations and $k_{IBA,\phi}$ equals $k_{IBA}(1 - \phi)$.

The intrinsic rate constant is determined from the concentrations of the reactants at the site of the reaction. In microemulsion media, the site of the reaction is the Stern layer and neither the bulk overall nor the phase volume corrected concentrations are truly applicable for the determination of intrinsic rate constants. It is almost certain that the concentrations of catalyst and substrate are different in the Stern layer (SL). The intrinsic rate constant is defined in

$$d[PNDP]_{SL}/dt = -k_2[PNDP]_{SL}[IBA]_{SL} \quad (3)$$

where the subscript SL denotes Stern layer. Unfortunately, there is no way to measure or estimate $[PNDP]_{SL}$ or $[IBA]_{SL}$. However, the phase-corrected concentrations are proportional to the Stern layer concentrations. Hence, even though we cannot obtain absolute values of k_2, we are able to determine relative values, which, for our purposes, are very useful. The phase-corrected rate constants are not intrinsic rate constants, but they can be used in the determination of microdroplet surface potential.

In order to compare the phase volume corrected second-order rate constants in different microemulsions, data must be available from comparable regions of the pertinent phase maps. We used the microemulsion media CTAB, CTAC 1.1, CTAC DBF 1.0, and Brij 96.[8] The compositions of the microemulsion were systematically varied by titration with aqueous buffer at constant emulsifier to oil ratio. The exact microemulsion compositions in which these studies were conducted and the corresponding values

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TABLE IX: Data for Various Aqueous Phase Percentages at Constant Oil/Emulsifier Ratio[a]

% surfactant	% cosurfactant	% aqueous	% oil	pH	k_{IBA}, $(M{\cdot}s)^{-1}$	$k_{IBA,\varphi}$, $(M{\cdot}s)^{-1}$	$10^{-1}\psi$, mV
CTAC	Adogen						
18.6	16.5	58.5	6.4	8.68	9.43	5.52	8.52
16.1	14.4	64.0	5.6	8.77	10.05	6.43	8.90
14.0	12.5	70.0	3.5	9.35	9.43	6.60	8.97
11.7	10.3	75.0	3.0	8.73	11.9	8.93	9.74
9.54	8.46	80.0	2.0	8.76	12.83	10.3	10.11
CTAG	BuOH						
35.0	35.0	25.0	5.0	9.5	0.97	0.242	0.489
28.0	28.0	40.0	4.0	9.32	0.941	0.376	1.62
22.5	22.5	50.0	5.0	9.5	1.22	0.610	2.86
18.0	18.0	60.0	4.0	9.5	1.22	0.732	3.33
15.5	15.5	65.0	3.0	8.97	1.55	1.01	4.15
9.0	9.0	80.0	2.0	8.7–10.4	3.26	2.61	6.59
CTAC	DbF						
24.2	24.2	43.4	8.0	8.59	4.68	2.03	5.94
16.9	16.9	56.0	10.0	8.45	5.46	3.06	6.99
11.5	11.5	73.0	4.0	8.69	6.86	5.01	8.26
Brij 96	BuOH						
20.5	20.5	55.0	4.0	9.85	0.329	0.181	N/A
15.5	15.5	65.0	3.0	8.30	0.259	0.168	
13.5	13.5	70.0	3.0	9.60	0.340	0.238	
11.6	11.6	75.0	3.0	8.83	0.320	0.240	
9.0	9.0	80.0	2.0	8.97	0.283	0.226	

[a] Aqueous phase is 0.03 M borate buffer. Oil phase is hexadecane. Surfactant and cosurfactant are indicated.

of k_{IBA} and $k_{IBA,\phi}$ are presented in Table IX.

All of the expected trends are obvious: The k_{IBA} values in cationic microemulsion are higher than in nonionic microemulsion; the k_{IBA} values increase as cosurfactant polarity increases; and increase in the aqueous phase volume $(1 - \phi)$ generally causes an increase in k_{IBA}. The same trends are obvious in the phase corrected constants, $k_{IBA,\phi}$. Plots of $k_{IBA,\phi}$ vs aqueous phase volume $(1 - \phi)$ are shown in Figure 6. For the three cationic microemulsions, $k_{IBA,\phi}$ increases significantly with increase in $(1 - \phi)$; for Brij 96 microemulsions, $k_{IBA,\phi}$ is virtually independent of $(1 - \phi)$. These results indicate that the charge buildup at the microdroplet in Brij 96 microemulsions is negligible.

Based upon the above discussion, phase-corrected rate constants obtained in cationic microemulsions can meaningfully be compared to the rate constants obtained in Brij 96 microemulsions. Following Mackay and Hermansky[8] it can be shown that

$$\frac{(k_{IBA,\phi})_{\mathrm{cationic}\mu\mathrm{E}}}{(k_{IBA,\phi})_{\mathrm{Brij96}\mu\mathrm{E}}} = \frac{k_{2,\mathrm{cationic}\mu\mathrm{E}}}{k_{2,\mathrm{Brij}\mu\mathrm{E}}}$$

$$= \exp\{-e/kT\}\{\Psi_{\mathrm{cationic}} - \Psi_{\mathrm{Brij}}\}$$

And if $\Psi_{\mathrm{Brij}} \sim 0$

$$\frac{(k_{IBA,\phi})_{\mathrm{cationic}\mu\mathrm{E}}}{(k_{IBA,\phi})_{\mathrm{Brij}\mu\mathrm{E}}} = \exp\{-e\Psi_{\mathrm{cationic}}/kT\} \tag{4}$$

where e, k, and T are the charge on the electron, the Boltzmann constant, and absolute temperature, respectively. Equation 4 was used to estimate the surface potential, Ψ, of the microdroplets in the cationic microemulsions. The data are presented in Table IX. In a model which assumes that the catalysis is due to an electrostatically enhanced concentration of substrate and catalyst, it is not surprising to see that the calculated values increase with $k_{IBA,\phi}$. In order to test the applicability of the surface potential model, other properties related to Ψ must be studied.

Figure 6 shows that the values of $k_{IBA,\phi}$ in the cationic microemulsions change dramatically with aqueous phase volume $(1 - \phi)$; the values of $k_{IBA,\Psi}$ in the Brij 96 microemulsion are virtually independent of aqueous phase volume. These results are very similar to those reported by Mackay and Hermansky[8] in their investigation of the hydrolysis of phosphate esters in a CTAB/1-butanol microemulsions in the presence of the nucleophiles F^- and OH^-.

The fact that $k_{IBA,\phi}$ increases sharply with increasing aqueous volume fraction suggests that inorganic counterions Cl^- and Br^- are removed from the Stern layer as the fraction of water increases. This must result in the enhancement of charge and surface potential. Due to the fact that IBA is an organic anion, its electric potential energy minimum may occur in the Stern layer where the dielectric constant may lie in the range of 2–78. The enhancement of the charge on the microdroplet surface by removal of Cl^- and Br^- causes the concentration of IBA in the Stern layer to increase and the rate constants $k_{IBA,\phi}$ to rise sharply with the aqueous volume fraction.

Conclusions

Microemulsions containing the hydrotrope Adogen 464 in place of neutral cosurfactant exhibit higher rates of phosphate ester hydrolysis due to increased surface charge and thus higher effective anionic nucleophile concentrations. The rate constants for ester hydrolysis increase in the order: 1-butanol < *N*,*N*-dibutylformamide < Adogen 464. The rate constants for various IBA derivatives in microemulsions do not completely follow the order of electron-withdrawing power of the substituents exhibited in homogeneous or simple micellar solutions. The reason for this behavior is not understood at present.

Registry No. PNDP, 10359-36-1; OIBA, 112391-40-9; IBA, 304-91-6; NIBA, 23330-00-9; CIBA, 114692-22-7; PNIBA, 112391-34-1; IBX, 114692-23-8.