

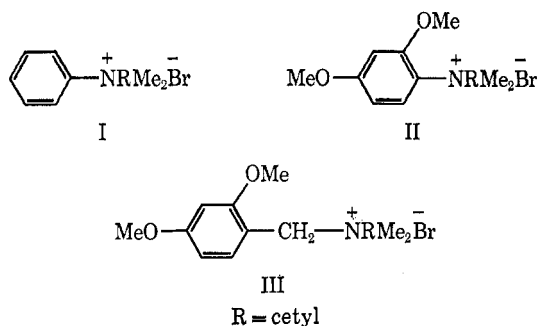
Structural Effects upon Catalysis by Cationic Micelles<sup>1</sup>C. A. BUNTON, L. ROBINSON, AND L. SEPULVEDA<sup>2</sup>

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The catalytic efficiencies of phenyl- and 2,4-dimethoxyphenylcetyltrimethylammonium bromides (CPDA and CDPDA) are greater than that of cetyltrimethylammonium bromide (CTABr) for the spontaneous hydrolyses of the dianions of 2,4- and 2,6-dinitrophenyl phosphates, the reactions of hydroxide and fluoride ions with *p*-nitrophenyl diphenyl phosphate, and the reaction of hydroxide ion with 2,4-dinitrochlorobenzene in water, because of more efficient micelle-substrate binding. There is little effect upon the rate in the micellar phase. 2,4-Dimethoxybenzylcetyltrimethylammonium bromide (CDBDA) is an even better catalyst for the spontaneous hydrolysis of 2,4-dinitrophenyl phosphate, but not for the other reactions, probably because of its low solubility in water.

Cationic micelles of long-chain alkyl trimethylammonium ions are effective catalysts of reactions between uncharged substrates and anionic nucleophiles,<sup>3-7</sup> and micelles of cetyltrimethylammonium bromide are also effective catalysts of the spontaneous hydrolysis of 2,4- and 2,6-dinitrophenyl phosphates.<sup>8</sup> The intent of much of this work has been to find models for enzymic reactions, and although clear analogies can be drawn between the two systems, the high specificity of most enzymic reactions contrasts sharply with the generally low specificity of micellar catalysts.<sup>3-5,8,9-11</sup> For some micellar-catalyzed reactions, the catalysis increases with increasing length of the alkyl chain, but there has been little study of the effect of changes in the hydrophilic ionic residue of the detergent.<sup>12</sup> The substrates which we have used in micellar-catalyzed reactions contain nitrophenyl groups and were chosen because they gave easily detectable nitrophenols as reaction products, and the present work was undertaken in the hope that the introduction of electron-rich aryl groups into the hydrophilic end group of the cationic detergent would assist the binding of these substrates to the micelle and increase the catalytic efficiency of the detergent. Three quaternary ammonium salts were therefore prepared: phenylcetyltrimethylammonium bromide, CPDA (I); 2,4-dimethoxyphenylcetyltrimethylammonium bromide, CDPDA (II); and 2,4-dimethoxybenzylcetyltrimethylammonium bromide, CDBDA (III).



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(2) Chile-California Cooperative Program Fellow on leave from the Faculty of Chemistry and Pharmacy, the University of Chile, Santiago.

(3) F. M. Menger and C. E. Portnoy, *J. Amer. Chem. Soc.*, **89**, 4698 (1967), and references cited therein.

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(5) C. Gitler and A. Ochoa-Solano, *ibid.*, **90**, 5004 (1968).

(6) C. A. Bunton and L. Robinson, *ibid.*, **90**, 5972 (1968).

(7) C. A. Bunton and L. Robinson, *J. Org. Chem.*, **34**, 773, 780 (1969); C. A. Bunton, L. Robinson, and L. Sepulveda, *J. Amer. Chem. Soc.*, **91**, 4813 (1969).

The reactions examined were the spontaneous hydrolyses of 2,4- and 2,6-dinitrophenyl phosphate,<sup>8</sup> and the attack of hydroxide ion on 2,4-dinitrochlorobenzene<sup>9</sup> and of hydroxide or fluoride ion on *p*-nitrophenyldiphenyl phosphate<sup>7</sup> in water.

## Experimental Section

**Materials.**—The preparation and purification of the substrates has been described.<sup>5-8</sup> Dimethylaniline was distilled before use, recrystallized 2,4-dimethoxyaniline (Aldrich) was dimethylated with Me<sub>2</sub>SO,<sup>13</sup> and the product was purified by steam distillation. 2,4-Dimethoxybenzoic acid was converted into the acid chloride using SOCl<sub>2</sub>, the acid chloride was converted into the dimethylamide using dimethylamine, and the amide was reduced with LiAlH<sub>4</sub><sup>14</sup> to give 2,4-dimethoxybenzyltrimethylamine, which was purified by vacuum distillation [bp 127° (6 Torr)]. The tertiary amines were then refluxed for 24 hr with cetyl bromide in EtOH. CPDA (I) and CDPDA (II) were isolated by adding ether and were purified by several recrystallizations from ether-EtOH. The phenyl derivative, CPDA (I), had mp 116–118°, and gave a quantitative amount of the dichromate salt when treated with K<sub>2</sub>CrO<sub>7</sub>.<sup>15</sup>

*Anal.* Calcd for I: C, 67.6; H, 10.3; N, 3.3; Br, 18.8. Found: C, 67.4; H, 10.3; N, 3.3; Br, 18.6.

The dimethoxyphenyl derivative, CDPDA (II), had mp 103–105° and gave a quantitative yield of its dichromate.

*Anal.* Calcd for II: C, 63.4; H, 9.9; N, 2.9; Br, 16.5. Found: C, 63.5; H, 9.9; N, 2.9; Br, 16.6.

We were unable to obtain a crystalline bromide of the dimethoxybenzyl derivative, CDBDA (III), and therefore treated it with LiClO<sub>4</sub> to obtain the perchlorate, mp 88.5–90.5°.

*Anal.* Calcd for III perchlorate: C, 62.3; H, 9.6; N, 2.7. Found: C, 62.3; H, 9.7; N, 2.6.

The bromide was obtained by evaporating the ether and ethanol *in vacuo*. The gummy bromide was then washed several times with hexane and dried in a vacuum oven at 80° for 5 days. It contained 15.6% inorganic bromide (theory 16.0%).

**Critical Micelle Concentrations.**—The values obtained conductimetrically, in water at 25.0°, follow: CPDABr (I), 2.7 × 10<sup>-4</sup> M; CDPDABr (II), 0.9 × 10<sup>-4</sup> M; and CDBDABr (III), 1.8 × 10<sup>-4</sup> M. These values were lower than that of 7.8 × 10<sup>-4</sup> M for cetyltrimethylammonium bromide (CTABr).<sup>5,8,16</sup> The solutions of CDBDABr were turbid, except at very low concentration, and hence we cannot place reliance on the value for this detergent.

**Kinetics.**—The rate constants, *k<sub>p</sub>*, in sec<sup>-1</sup>, were measured spectrophotometrically.<sup>6-8</sup> The dinitrophenyl phosphates were

(8) C. A. Bunton, E. J. Fendler, L. Sepulveda, and K-U. Yang, *ibid.*, **90**, 5512 (1968).

(9) D. G. Herries, W. Bishop, and F. M. Richards, *J. Phys. Chem.*, **68**, 1842 (1964).

(10) T. C. Bruice, J. Katzhendler, and L. R. Fedor, *ibid.*, **71**, 1961 (1967); T. C. Bruice, J. Katzhendler, and L. R. Fedor, *J. Amer. Chem. Soc.*, **90**, 1333 (1968).

(11) T. E. Wagner, C. Hsu, and C. S. Pratt, *ibid.*, **89**, 6366 (1967).

(12) J. L. Kurz, *J. Phys. Chem.*, **66**, 2239 (1962).

(13) H. Gilman and I. Banner, *J. Amer. Chem. Soc.*, **62**, 344 (1940).

(14) A. C. Cope and E. Ciganek, "Organic Syntheses," Coll. Vol. IV, John Wiley & Sons, Inc., New York, N. Y., 1963, p 339.

(15) S. R. Epton, *Trans. Faraday Soc.*, **44**, 226 (1948).

(16) T. Nash, *J. Appl. Chem. (London)*, **8**, 440 (1958).

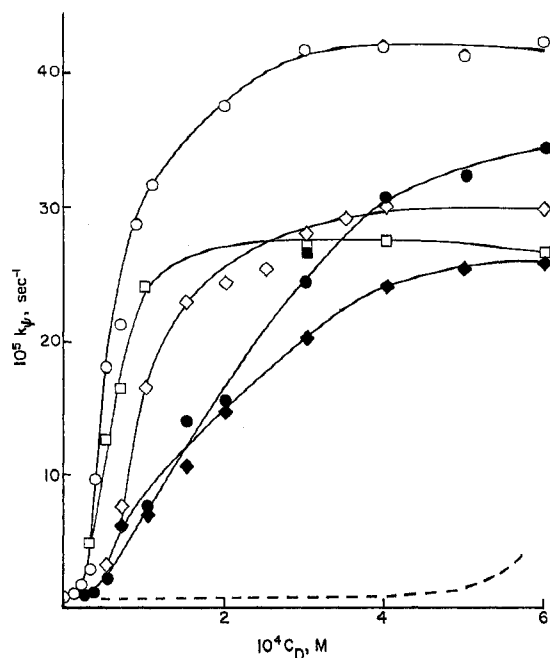


Figure 1.—Detergent effects upon the spontaneous hydrolysis of 2,4-dinitrophenyl phosphate dianion at pH 9.0 and 25.0° [the broken line is interpolated from the rate constants in CTABr (ref 8)]:  $\diamond$ ,  $1.8 \times 10^{-5} M$  substrate in CPDA;  $\blacklozenge$ ,  $9.4 \times 10^{-5} M$  substrate in CPDA;  $\square$ ,  $1.8 \times 10^{-5} M$  substrate in CDPDA;  $\blacksquare$ ,  $1.8 \times 10^{-5} M$  sodium salt of the substrate in CDPDA;  $\circ$ ,  $1.8 \times 10^{-5} M$  substrate in CDBDA;  $\bullet$ ,  $9.4 \times 10^{-5} M$  substrate in CDBDA.

generally used as their cyclohexylamine salts, but in a few experiments were converted into the sodium salts using ion-exchange resin, with little change in the value of  $k_p$ . Added cyclohexylamine had very little effect on the micellar-catalyzed hydrolyses of the dinitrophenyl phosphates. The detergents were added as the bromides.

**Phase Separations.**—Solutions of the dimethoxybenzyl derivative CDBDA (III) were turbid, even at concentrations below the apparent critical micelle concentration, and the turbidity did not disappear at temperatures up to 100°. There was no turbidity with the other bromides, but a solution of the dimethoxyphenyl derivative CDPDA (II) became turbid when 0.2 M NaNO<sub>3</sub> was added; however, this turbidity disappeared on heating; and the upper consolute temperature<sup>17,18</sup> was 31.9°.

We attempted to obtain some evidence on the nature of the turbid aqueous suspension of the dimethoxybenzyl derivative (CDBDA) by filtering a  $1 \times 10^{-3} M$  suspension through a 0.45- $\mu$  Millipore filter. The clear filtrate contained a  $0.78 \times 10^{-3} M$  concentration of detergent, and the solid particles as seen through a Reichert microscope were approximately spherical and 1–2  $\mu$  in diameter. (If we assume that the density of the particles was ca. 1 g/ml, each of these particles would contain 1–10  $\times 10^6$  molecules of detergent.) We also added 2,4-dinitrophenyl phosphate to this detergent in  $2.5 \times 10^{-3} M$  borate buffer in order to examine its uptake by these large particles. Filtration through a 0.45- $\mu$  Millipore filter gave a clear solution of  $1.02 \times 10^{-4} M$  2,4-dinitrophenyl phosphate (determined spectrophotometrically at 358 m $\mu$  after complete hydrolysis). The original solution contained a  $1.36 \times 10^{-4} M$  concentration of 2,4-dinitrophenyl phosphate, so that a  $0.34 \times 10^{-4} M$  concentration was in the particles retained by the filter. The filter retained a  $2.2 \times 10^{-4} M$  concentration of the detergent, so that ca. one 2,4-dinitrophenyl phosphate ion was taken up by ten ions of the detergent.

## Results

### Phase Diagram for 2,4-Dimethoxyphenylcetyltrimethylammonium Ion.—No cloud points were found

(17) R. R. Balmбра, J. S. Clunie, J. M. Corkill, and J. F. Goodman, *Trans. Faraday Soc.*, **58**, 1661 (1962).

(18) L. Sepulveda and F. MacRitchie, *J. Colloid Interfac. Sci.*, **28**, 19 (1968).

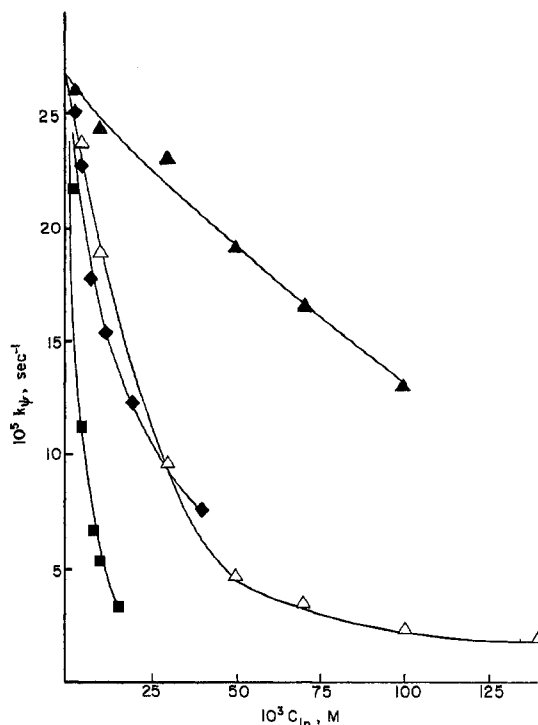


Figure 2.—Salt effects upon the hydrolysis of 2,4-dinitrophenyl phosphate dianion at 25.0° in CDPDA at pH 9.0:  $\blacktriangle$ , NaCl;  $\triangle$ , NaNO<sub>3</sub>;  $\diamond$ , C<sub>6</sub>H<sub>5</sub>OPO<sub>3</sub>Na<sub>2</sub>;  $\blacksquare$ , NaOTs.

with the bromide of this detergent, but they appeared when 0.2 M sodium nitrate was present. The requirement for the existence of an upper consolute temperature is that there is a positive enthalpy of mixing, such that  $\partial^2 \Delta H^E / \partial X_2^2 < 0$ <sup>17–19</sup> (where  $\Delta H^E$  is the excess molar enthalpy of mixing, and  $X_2$  is the mole fraction of the detergent), because the net water–water interactions and the detergent–detergent interactions are stronger than those between water and detergent. The salting out of the detergent by sodium nitrate means that nitrate ion associates more strongly with the quaternary ammonium ion than does the bromide ion, and so is more effective at excluding water molecules from the micellar phase. Consistently, nitrate ions are very effective inhibitors of catalysis by cationic micelles.<sup>6–8</sup> We found no phase separation when 0.2 M sodium nitrate was added to 0.1 M CTABr even at 0°, but phase separation was observed with phenylcetyltrimethylammonium bromide (CPDABr, I), although this system was not studied quantitatively.

**Kinetics. Hydrolysis of 2,4-Dinitrophenyl Phosphate.**—The values of  $k_p$  for the spontaneous hydrolysis of 2,4-dinitrophenyl phosphate in the presence of the various detergents are given in Figure 1. The values of  $k_p$  are sensitive to substrate concentration and increase much more steeply with detergent concentration when the substrate concentration is  $1.8 \times 10^{-5} M$  than when it is  $9.4 \times 10^{-5} M$  and therefore not much smaller than the detergent concentration.

Salt effects upon the catalysis by the dimethoxyphenyl derivative (CDPDA) are shown in Figure 2 for 2,4-dinitrophenyl phosphate. The salt order, no salt > NaCl > NaNO<sub>3</sub>  $\cong$  PhOPO<sub>3</sub>Na<sub>2</sub> > NaOTs, is that generally found for reactions catalyzed by cationic

(19) I. Prigogine and R. DeFay, "Chemical Thermodynamics," Longmans, Green and Co., London, 1954, p 286.

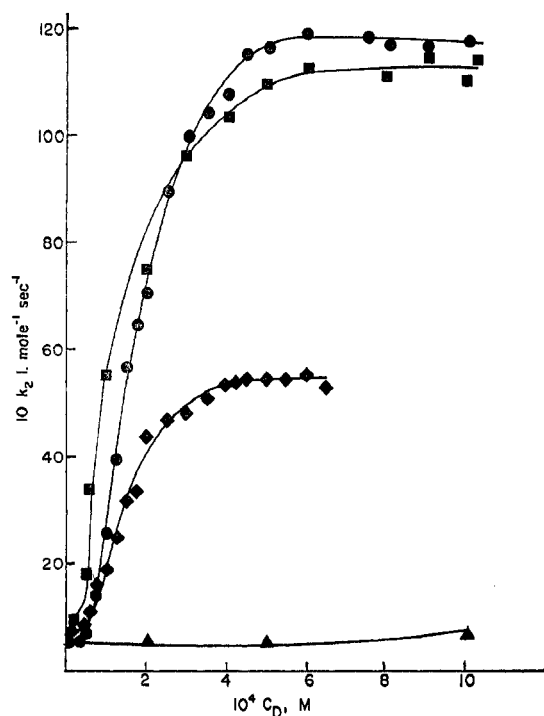


Figure 3.—Detergent effects upon the reaction of hydroxide ion with *p*-nitrophenyldiphenyl phosphate at 25.0°: ●, CPDA; ■, CDPDA; ◆, CDBDA; ▲, CTABr (ref 7).

detergents, and depends upon the charge density of the ion.<sup>4,6-8</sup>

A few runs were made with 2,6-dinitrophenyl phosphate, and the results are given in Table I. Inhibition by benzoate ion is shown by the results in Table II. A similar inhibition by benzoate ion had been found for the CTA catalysis.<sup>8</sup>

TABLE I  
HYDROLYSIS OF 2,6-DINITROPHENYL PHOSPHATE IN  
2,4-DIMETHOXYPHENYLCELYLDIMETHYLAMMONIUM BROMIDE<sup>a</sup>

Concn of detergent × 10 <sup>4</sup> , M	$k_{\psi} \times 10^4$ , sec <sup>-1</sup>	
	0.45	
0.50	0.75	0.90 <sup>b</sup>
0.70	0.92	1.58 <sup>b</sup>
1.00	1.49	
1.50	2.61	3.88 <sup>b</sup>
2.00	3.68	6.37 <sup>b</sup>
2.50	4.66	7.90 <sup>b</sup>
3.00	6.06	...
3.50	6.40	8.84 <sup>b</sup>
5.00	7.83	8.66 <sup>b</sup>
7.00	8.22	9.36 <sup>b</sup>
8.00	...	9.70 <sup>b</sup>
9.00	8.96	9.70 <sup>b</sup>
10.0	9.41	
20.0	9.78	
30.0	10.3	

<sup>a</sup> At 25.0° with  $9.4 \times 10^{-5}$  M cyclohexylamine salt of the substrate at pH 9.0 and  $2.5 \times 10^{-3}$  M borate buffer. <sup>b</sup>  $1.8 \times 10^{-5}$  M substrate. With CTABr the maximum value of  $k_{\psi} = 12 \times 10^{-4}$  sec<sup>-1</sup> (ref 8).

**Nucleophilic Substitutions.**—The second-order rate constants for attack of hydroxide ion upon *p*-nitrophenyldiphenyl phosphate at 25.0° are shown in Figure 3, together with values obtained earlier using concentra-

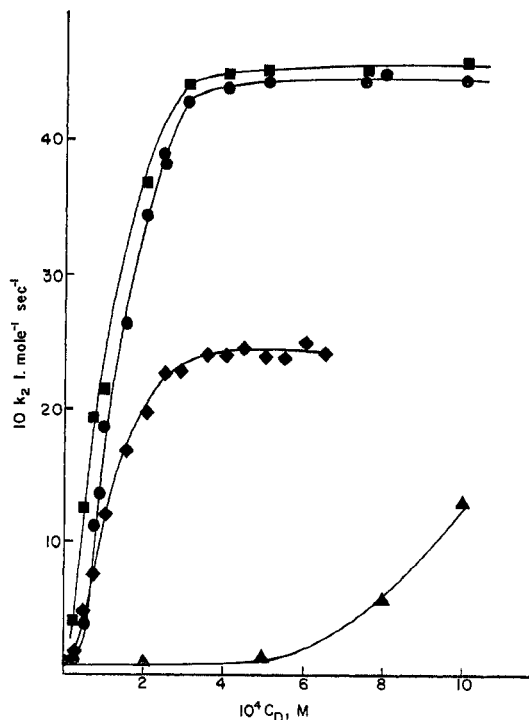


Figure 4.—Detergent effects upon the reaction of fluoride ion with *p*-nitrophenyldiphenyl phosphate at 25.0° and pH 9.0: ●, CPDA; ■, CDPDA; ◆, CDBDA; ▲, CTABr (ref 7).

TABLE II  
BENZOATE ION INHIBITION OF THE DETERGENT-CATALYZED  
HYDROLYSIS OF 2,6-DINITROPHENYL PHOSPHATE<sup>a</sup>

Concn of NaOBz × 10 <sup>2</sup> , M	$k_{\psi} \times 10^4$ , sec <sup>-1</sup>
	9.70
0.10	6.85
0.30	2.96
0.50	2.32
0.80	1.56
1.20	0.77
2.00	0.62
3.00	0.56

<sup>a</sup> At 25.0° with  $1.75 \times 10^{-5}$  M substrate at pH 9.0 in  $2.5 \times 10^{-3}$  M borate buffer and  $8 \times 10^{-4}$  M 2,4-dimethoxyphenylcetyl-dimethylammonium bromide (CDPDA).

tions of CTABr.<sup>7</sup> Similar results for the attack of fluoride ion at 25.0° are given in Figure 4. The results of experiments at other temperatures and at low and high detergent concentrations are given in Tables III and IV.

The Arrhenius equation is followed for the attack of fluoride ion upon *p*-nitrophenyldiphenyl phosphate catalyzed by CPDA and CDPDA. For both detergents,  $E = 11$  kcal/mol and  $\log A = 8.5$  (calculated for 1 M reagents), with  $c = 0.0005$  M in the plateau region. The activation energy is therefore lower than the corresponding values of 13.6 kcal/mol for attack of hydroxide ion and 14.0 kcal/mol for attack of fluoride ion for the CTABr-catalyzed reaction.<sup>7</sup>

However, the Arrhenius equation is not obeyed for the reaction between hydroxide ion and *p*-nitrophenyldiphenyl phosphate catalyzed by CPDA and CDPDA. For both detergents,  $E \cong 11$  kcal/mol in the range of 5.0–15.4° and 16 kcal/mol in the range of 15.4–25.0°. The Arrhenius equation could fail because of tempera-

TABLE III

DETERGENT EFFECTS ON THE REACTION OF HYDROXIDE ION WITH *p*-NITROPHENYLDIPHENYL PHOSPHATE<sup>a</sup>

Detergent	Concn of detergent × 10 <sup>4</sup> , M	5.0°	15.4°	25.0°	30.9°
CPDA	1.29	2.63	4.83	7.72	
	0.50	1.62	3.01	7.00	
	5.00	23.2	45.9	116	
	10.0	22.9	45.0	117	
CDPDA	0.50	4.50	8.80	19.2	
	6.00	22.9	47.6	112	
	12.0	23.0	46.5	114	
CDBDA	18.0	21.5	48.2	110	
	5.0		28.8	54.3	84.4
CTABr	6.0		28.9	55.5	84.6
	30.0	10 <sup>b</sup>	28 <sup>b</sup>	56 <sup>b</sup>	

<sup>a</sup> Values of  $k_2 \times 10$  in l. mol<sup>-1</sup> sec<sup>-1</sup>, with 0.01 M NaOH. <sup>b</sup> Reference 7.

TABLE IV

DETERGENT EFFECTS ON THE REACTION OF FLUORIDE ION WITH *p*-NITROPHENYLDIPHENYL PHOSPHATE<sup>a</sup>

Detergent	Concn of detergent × 10 <sup>4</sup> , M	5.0°	15.4°	25.0°	30.9°
CPDA	...	0.23	0.53	1.05	1.62
	0.50	0.29	1.07	3.71	
	5.00	11.7	25.3	44.5	
CDPDA	10.0	11.9	25.4	44.6	
	0.50	...	...	12.5	
	5.00	12.4	25.7	45.2	
	10.0	...	...	46.0	
CDBDA	12.0	12.0	26.0	44.2	
	5.00		14.5	24.0	36.8
CTABr	6.00		13.6	25.0	36.8
	20.0	5 <sup>b</sup>	16 <sup>b</sup>	34 <sup>b</sup>	

<sup>a</sup> Values of  $k_2 \times 10$  in l. mol<sup>-1</sup> sec<sup>-1</sup> with 0.01 M NaF in 0.015 M sodium borate, pH 9. <sup>b</sup> Reference 7.

ture effects upon the properties of the micelles, *e.g.*, critical micelle concentration or aggregation number, but it is surprising that the equation is obeyed for the attack of fluoride but not hydroxide ion, suggesting that the nucleophilic anion may be affecting the relation between temperature and micellar properties.

The detergent catalysis is inhibited by added salts, and the salt effects are shown in Tables V and VI. The salt effects depend upon the bulk of the anion, as is generally found.<sup>4,6-8</sup>

The second-order rate constants for the reaction between 2,4-dinitrochlorobenzene and hydroxide ion catalyzed by the cetyl ammonium bromides are shown in Figure 5.

For the bimolecular nucleophilic substitutions, the maximum values of the rate constants observed with 2,4-dimethoxybenzylcetyldimethylammonium bromide (CDBDA) are generally less than those observed with the phenylammonium bromides (CPDA and CDPDA), probably because it exists in part as large particles, which should be less catalytically effective on a mole to mole basis than micelles for attack of an ionic nucleophile on a substrate molecule on the surface. For the spontaneous hydrolysis of the dinitrophenyl phosphate anions, 2,4-dimethoxybenzylcetyldimethylammonium bromide is a good catalyst, and we know that 2,4-dinitrophenyl phosphate dianion is incorporated into the large particles, suggesting that this spontaneous reaction can occur on the colloidal particles as well as in the

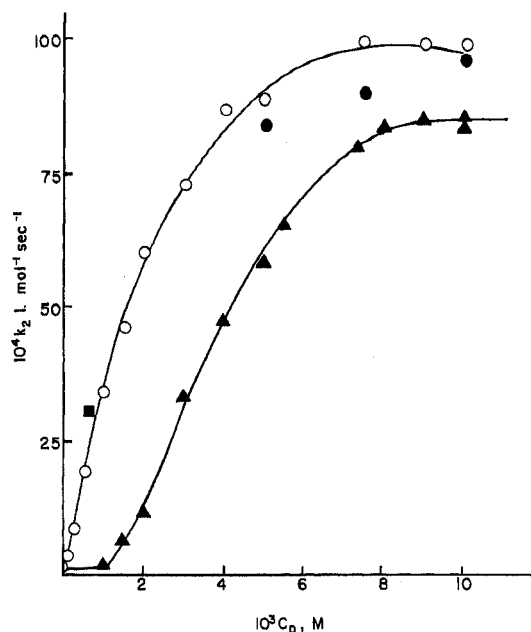


Figure 5.—Detergent effects upon the reaction of hydroxide ion with 2,4-dinitrochlorobenzene at 25.0°: O, CPDA; ●, CDPDA; ■, CDBDA; ▲, CTABr (ref 6).

TABLE V

SALT EFFECTS ON THE REACTION OF HYDROXIDE ION WITH *p*-NITROPHENYLDIPHENYL PHOSPHATE<sup>a</sup>

Salt	Concn of salt, M	Detergent		
		CPDA <sup>b</sup>	CDPDA <sup>b</sup>	CDBDA <sup>c</sup>
...	...	117	111	53.3
NaCl	0.010	46.6	56.6	32.2
NaCl	0.020	31.8	37.8	23.3
NaCl	0.040	19.9	22.9	12.3
CH <sub>3</sub> SO <sub>3</sub> Na	0.010	59.3	55.2	30.7
CH <sub>3</sub> SO <sub>3</sub> Na	0.020	38.4	37.5	18.5
CH <sub>3</sub> SO <sub>3</sub> Na	0.040	23.2	24.7	14.6
NaBr	0.010	22.2	28.8	10.9
NaBr	0.020	13.4	18.0	4.83
NaBr	0.040	7.00	9.30	2.95
NaNO <sub>2</sub>	0.005	...	...	10.2
NaNO <sub>2</sub>	0.010	15.9	19.9	5.83
NaNO <sub>2</sub>	0.020	8.90	11.1	...
NaNO <sub>2</sub>	0.040	4.54	6.10	...
PhOPO <sub>2</sub> Na <sub>2</sub>	0.005	19.2	18.3	14.8
PhOPO <sub>2</sub> Na <sub>2</sub>	0.020	11.9	9.00	10.6
<i>p</i> - <i>t</i> -BuC <sub>8</sub> H <sub>4</sub> OPO <sub>2</sub> Na <sub>2</sub>	0.0025	...	8.40	...
NaOTs	0.0002	...	...	19.6
NaOTs	0.0005	...	...	13.7
NaOTs	0.001	31.5	36.4	5.40
NaOTs	0.00015	...	...	3.82
NaOTs	0.005	7.11	9.40	...
NaOTs	0.010	3.31	5.79	...
NaOTs	0.020	2.47	3.49	...
			8.4	

<sup>a</sup> Values of  $k_2 \times 10$  in l. mol<sup>-1</sup> sec<sup>-1</sup> at 25.0° with 0.01 M sodium hydroxide. <sup>b</sup> 0.0008 M detergent. <sup>c</sup> 0.0004 M detergent.

micellar phase, although this would not be so for bimolecular attack by an external nucleophile. It is also possible that all the reaction occurs in the micellar phase, and that the micelles of this detergent are very good catalysts for the spontaneous reaction.

### Discussion

**Kinetic Form of the Catalysis.**—Micellar catalysis is generally treated on the assumption that the substrate,

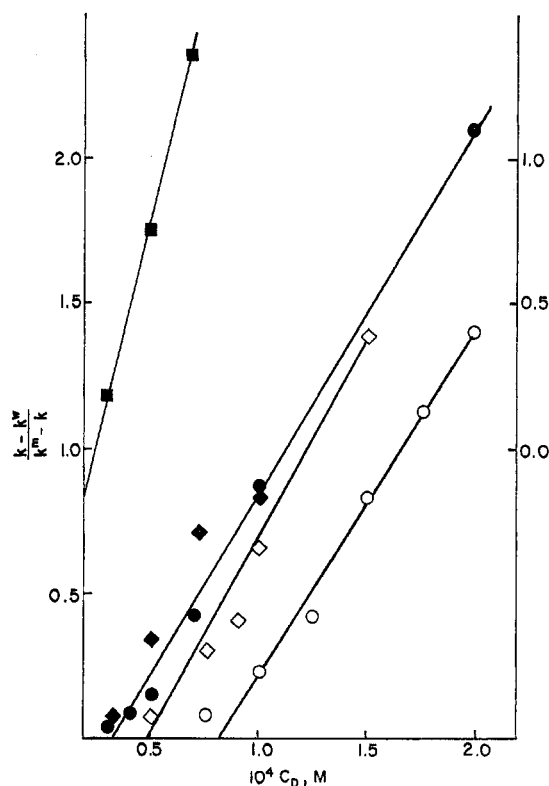


Figure 6.—Values of  $(k - k^w)/(k^m - k)$  vs. detergent concentration at 25.0° (solid points refer to CDPDA, open points to CPDA): ■, 2,4-dinitrophenyl phosphate; ●, *p*-nitrophenyldiphenyl phosphate with OH<sup>-</sup>; ◆, *p*-nitrophenyldiphenyl phosphate with F<sup>-</sup>. The left-hand scale refers to the reactions of *p*-nitrophenyldiphenyl phosphate, and the right-hand scale to those of 2,4-dinitrophenyl phosphate.

TABLE VI  
SALT EFFECTS ON THE REACTION OF FLUORIDE ION  
WITH *p*-NITROPHENYLDIPHENYL PHOSPHATE<sup>a</sup>

Salt	Concn of salt, M	Detergent		
		CPDA <sup>b</sup>	CDPDA <sup>b</sup>	CDBDA <sup>c</sup>
...	...	45.2	44.7	23.9
NaCl	0.010	27.5	27.3	14.2
NaCl	0.020	20.4	19.5	11.0
NaCl	0.040	12.6	12.1	6.42
CH <sub>3</sub> SO <sub>3</sub> Na	0.020	24.6	20.5	12.0
CH <sub>3</sub> SO <sub>3</sub> Na	0.040	16.9	14.3	8.30
NaNO <sub>3</sub>	0.005	...	...	5.01
NaNO <sub>3</sub>	0.010	8.30	9.20	2.88
NaNO <sub>3</sub>	0.020	4.65	5.50	...
NaNO <sub>3</sub>	0.040	2.61	3.05	...
NaOTs	0.001	15.8	17.2	...
NaOTs	0.005	3.86	5.02	...
NaOTs	0.010	2.03	2.80	...
NaOTs	0.020	1.08	1.49	...

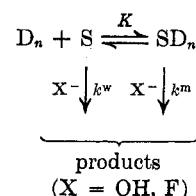
<sup>a</sup> Values of  $k_2 \times 10^1 \text{ mol}^{-1} \text{ sec}^{-1}$  at 25.0° with 0.01 M sodium fluoride at pH 9.0 in 0.015 M borate buffer. <sup>b</sup> 0.0008 M detergent. <sup>c</sup> 0.0004 M detergent.

S<sub>2</sub> can react in either the aqueous or micellar phase, and that there is an equilibrium between the substrate in the aqueous and micellar phases.<sup>3-9</sup> In the following formulation the micellized detergent is designated D<sub>n</sub>, and the concentration of micelles, c<sub>m</sub>, is given by eq 1,

$$c_m = (c_D - cmc)/N \quad (1)$$

where c<sub>D</sub> is the detergent concentration, N is the aggregation number of the micelle, and cmc is the critical micelle concentration.

The over-all reactions are then



where  $k^w$  and  $k^m$  are the first- or second-order rate constants for reactions in the aqueous and micellar phases, and for the spontaneous hydrolyses of the dinitrophenyl phosphate dianions the reagent does not enter into the rate equation.

The rate constant for the over-all reaction is given by eq 2. The kinetics of the various reactions fit eq 2 at

$$k = \frac{k^w + k^m K c_m}{1 + K c_m} \quad (2)$$

least qualitatively, because the rate constant,  $k$ , increases to an approximately constant value, which should be reached when  $K c_m \gg 1$  and  $k^m K c_m \gg k^w$ , and in the plateau region  $k$  should have the value of  $k^m$ . In a number of other anion-molecule reaction systems, the reaction rate increases to a maximum and then decreases with increasing detergent concentration,<sup>3,4,6-8</sup> and the difference between these systems is discussed later.

Equation 2 can be rearranged to give eq 3a or 3b.<sup>3,7</sup>

$$\frac{1}{k^w - k} = \frac{1}{k^w - k^m} + \frac{1}{(k^m - k^w)} \frac{N}{K(c_D - cmc)} \quad (3a)$$

$$\frac{k - k^w}{k^m - k} = \frac{K}{N} (c_D - cmc) \quad (3b)$$

Equation 3a is very useful in that it predicts that a plot of  $1/(k^w - k)$  against  $1/(c_D - cmc)$  should be linear,<sup>3</sup> and it allows the determination of both  $k^m$  and  $K/N$ . However, it is unsatisfactory for the treatment of the present data, because catalysis is observed at low detergent concentrations which are close to the critical micelle concentration, and therefore the value of  $1/(c_D - cmc)$  is very sensitive to the actual value used for the critical micelle concentration. Added solutes can promote micellization,<sup>3-8,10,20</sup> and therefore eq 3a should be used only when  $c_D \gg cmc$ . This condition is easily met in many detergent-catalyzed or detergent-inhibited reactions, but not in the present systems where catalysis is observed at detergent concentrations which are not much greater than those of the substrate. Therefore, we have used eq 3b, and plotted  $(k - k^w)/(k^m - k)$  vs.  $c_D$  (Figure 6). The value of  $k^m$  is assumed to be given by the value of  $k$  in the "plateau" region (Figures 2, 4, and 5). The disadvantage of using eq 3b is that there is a large uncertainty in the value of either the numerator or denominator when  $k \cong k^w$  or  $k \cong k^m$ , and only the rate constants in the steeply rising part of the curve are useful.

Some of the results are shown in Figure 6, and the intercepts on the horizontal axis should give the critical micelle concentration. The intercepts are, for the spontaneous hydrolysis of 2,4-dinitrophenyl phosphate,  $0.25 \times 10^{-4} M$ ; for the attack of hydroxide and fluoride ions upon *p*-nitrophenyldiphenyl phosphate,  $0.4 \times 10^{-4} M$  in CDPDA; and for the attack of hydroxide and fluoride ions upon *p*-nitrophenyldiphenyl phosphate in

CPDA,  $0.8 \times 10^{-4}$  and  $0.5 \times 10^{-4}$  M, respectively. These critical micelle concentration values are of the same order of magnitude as, but lower than, those determined in the absence of substrate and anionic nucleophiles which could promote micellization and decrease the value.<sup>3-8, 10, 20, 21</sup>

The slopes of the plots give values of  $K/N$  (Table VII). These values are only approximate because of

TABLE VII  
VALUES OF  $K/N$  DETERMINED KINETICALLY<sup>a</sup>

Substrate	Detergent		
	CPDA	CDPDA	CTABr
2,4-(NO <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> OPO <sub>3</sub> <sup>2-</sup>		$3 \times 10^4$	$1.8 \times 10^3$ <sup>d</sup>
<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> OPO(OPh) <sub>2</sub> <sup>b</sup>	$1.2 \times 10^4$	$1.2 \times 10^4$	
<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> OPO(OPh) <sub>2</sub> <sup>c</sup>	$1.3 \times 10^4$	$1.2 \times 10^4$	

<sup>a</sup> In water at 25.0°. <sup>b</sup> With OH<sup>-</sup>. <sup>c</sup> With F<sup>-</sup>. <sup>d</sup> Reference 8.

the approximations made in deriving eq 3b, and also because the sharp rate increase with a small change in detergent concentration makes it difficult to obtain enough data within the useful range of rate constants. Nonetheless, these values of  $K/N$  are much larger than those found earlier for the CTABr-catalyzed reactions.<sup>8</sup> We could not calculate  $K/N$  values for *p*-nitrophenyldiphenyl phosphate<sup>7</sup> because the hydrolysis in cationic micelles is too rapid even at low pH, but the much steeper rise of rate constant with detergent concentration for the aryl-substituted detergents, compared with CTABr (Figures 3 and 4), suggests that incorporation of substrate is much more efficient with the former.

The increase in the values of  $K/N$  over those for CTABr could arise either from better substrate-micelle binding, or from smaller aggregation numbers which would lead to more micelles for a given detergent concentration, or from the incorporation of more than one substrate molecule with a micelle. However, the general discussion is not affected by following the simplest assumption that a micelle incorporates only one substrate molecule.<sup>3</sup>

Various workers have noted that packing of the monomers in a spherical micelle is an important factor in determining the aggregation number, which should depend upon the length of the alkyl chain rather than upon the substituents on the hydrophilic head,<sup>22, 23</sup> and therefore there should be no large differences in the aggregation numbers for the various cetylammmonium detergents which we are using.

Aggregation numbers for a given micelle depend on electrolyte concentration, and should be lower in our kinetic solutions than the values determined in 0.3 M sodium chloride,<sup>21</sup> but it seems that these differences in  $K/N$  depend to a large extent on the enhanced binding of the substrate to the micelle. In 0.3 M sodium chloride,  $N = 63$  for CPDA and  $N = 43$  for CDPDA, from light-scattering measurements.<sup>24</sup> In our earlier work we assumed a value of  $N = 61$  for CTABr,<sup>6, 8</sup> whereas Behme and Cordes used a value of 100.<sup>25</sup> For

the spontaneous hydrolysis of 2,4-dinitrophenyl phosphate dianion, we therefore estimate  $K \cong 2 \times 10^6$  for CDPDA and  $K \cong 1-2 \times 10^5$  for CTABr<sup>8</sup> (depending upon the assumed value of  $N$ ). For the reaction of hydroxide or fluoride ion with *p*-nitrophenyldiphenyl phosphate, we calculate  $K \cong 5 \times 10^5$  for CPDA and  $1.7 \times 10^6$  for CDPDA.

We were unable to obtain  $K/N$  values for *p*-nitrophenyldiphenyl phosphate with CTABr either kinetically or by solubility measurements,<sup>7</sup> but the present results suggest that the aryl group enhances binding of a phosphate dianion to the micelle. The actual values of  $K$  depend upon the aggregation number,  $N$ , and to the extent that they may be too high we overestimate the strength of the binding of the substrate to the aryletyldimethylammonium micelle.

The 2,4-dimethoxy compound, CDBDA, is also very effective at binding the substrates, as shown by the steepness of the rate constant vs. detergent concentrations shown in Figures 1, 3, and 4, but for this compound estimation of binding constants would have little significance because of the presence of colloidal particles (see Results).

The greater binding of the substrates to these aryl compounds could result from aryl-aryl interactions, because we would expect the long alkyl side chains to be buried deeply in the interior of the micelles with the more polar aryl groups at the water-rich surface. However, the presence of the methoxy substituents does not markedly increase the binding, suggesting that the electron density of the aryl residue in the detergent is not a critical factor. Nauman and coworkers have noted that solubilization might be correlated with the number of voids on the micelle surface,<sup>23</sup> and this suggestion would seem to be very reasonable for those polar solutes which are known to reside in the water-rich exterior of the micelle.<sup>26</sup> The replacement of a methyl by an aryl group in the hydrophilic ammonium residue should increase these voids, *i.e.*, "roughen" the surface of the micelle. Experiments with aliphatic solutes and other detergents are needed to test between these two possibilities, but in any event it is clear that, as shown by Nauman and coworkers,<sup>23</sup> binding of solutes to a micelle of a given charge type is governed by the nature of the hydrophilic group as well as by the length of the hydrophobic chain.

The catalytic superiority of these aryldimethylammonium bromides over CTABr is least evident for the reaction between 2,4-dinitrochlorobenzene and hydroxide ion.<sup>6</sup> The reason for this may be that aryl-aryl attractions, while possibly assisting incorporation of the substrate into the micellar phase, may sterically hinder approach of the nucleophile. On the other hand, they should not shield the phosphoryl group of *p*-nitrophenyldiphenyl phosphate to nucleophilic attack, nor should they hinder the spontaneous dissociation of a dinitrophenyl phosphate dianion. However, these explanations ignore the possibility of substrate-micellar interactions changing the micellar structure in such a way that the catalytic power of the micelle will depend upon the substrate structure.

**Rate Constants in the Micellar Phase.**—Although aryl groups enhance substrate binding, they do not markedly affect the rate constants,  $k^m$ , for reaction in

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the micellar phase. This result is not particularly surprising, because aryl-aryl interactions between micelle and substrate in the initial state should also be present in the transition state for reaction in the micellar phase. In addition, for anion-molecule reactions, electrostatic interactions between the incoming nucleophile and the ammonium ions in the micelle are important in stabilizing the transition state, and a bulky aryl or benzyl group may hinder this interaction.

In many ion-molecule reactions catalyzed by ionic detergents, there are rate maxima with increasing detergent concentration,<sup>3,4,6,7</sup> and it has been suggested that these maxima occur when all the substrate is incorporated into the micelle, so that additional micelles then merely deactivate the ionic reagent<sup>6,7</sup> or, alternatively, that they result from a negative salt effect of the counterion.<sup>4</sup> We observed no rate maxima with these aryl-substituted detergents because the substrates are incorporated into the micellar phase at very low detergent concentrations, so that neither of these deactivation factors should be present.

**Analogies with Enzymic Catalysis.**—Many workers have noted formal similarities between micellar- and

enzyme-catalyzed reactions,<sup>3-5,9,10,27</sup> although in general it seems that micelles are best regarded as models for the binding between enzyme and substrate, except in the special cases in which active groups are built into the detergent.<sup>5,10,11</sup> The present results support this view, because they show that it is possible to vary the detergent structure so as to enhance the micelle-substrate binding without materially changing the rate constant for the reaction in the micellar phase.

**Registry No.**—2,6-Dinitrophenyl phosphate, 15732-00-0; 2,4-dimethoxyphenylcetyldimethylammonium bromide, 22040-11-5; *p*-nitrophenyldiphenyl phosphate, 10359-36-1.

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## Ease of Homolytic Dissociation of Sulfur-Sulfur Bonds. II. The Thermal Decomposition of Aryl $\alpha$ -Disulfones<sup>1</sup>

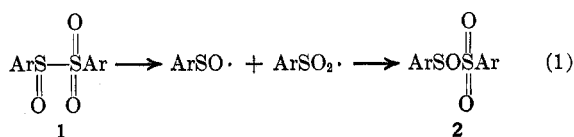
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The thermal decomposition of aryl  $\alpha$ -disulfones (**5**) has been studied in diglyme and bromobenzene at 145–165°. The decomposition follows good first-order kinetics, although the final reaction products are very complex. However, given such observations as the formation of a high yield of *sym*-tetraphenylethane when the decomposition is carried out in the presence of diphenylmethane, and the fact that  $\Delta S^\ddagger$  for the decomposition is large and positive (16.6 eu), the decomposition appears to involve initially the homolytic dissociation of the S-S bond in **5** (eq 2). Comparison of the rate and  $\Delta H^\ddagger$  for the decomposition of **5** with the same parameters for the thermal decomposition of aryl sulfinyl sulfones (**1**) shows that the sulfinyl sulfone decomposes *ca.*  $10^7$  times faster and has *ca.* 13 kcal/mol smaller  $\Delta H^\ddagger$ . This enormous difference in the ease of homolytic dissociation of **1** and **5** shows that the primary cause of the extremely facile radical dissociation of the sulfinyl sulfone is *not* destabilization of **1** due to repulsion between the two adjacent partially positively charged sulfur atoms. Comparison of the data for **1**, **5**, and other compounds containing a single S-S bond suggests that compounds in which a sulfinyl group is one of the partners in the S-S bond dissociate homolytically much more readily than those in which this feature is absent, and a likely reason for such behavior is suggested.

Aryl sulfinyl sulfones (**1**) undergo thermal decomposition very readily ( $t_{1/2} = 30$  min at 50°) *via* a process (eq 1) that involves an initial homolytic dissociation of the S-S bond in **1**, followed by a head-to-tail recombination of the resulting radical fragments to give the sulfonyl sulfonate **2**.<sup>1a</sup> The most striking thing about



the thermal decomposition of sulfinyl sulfones is the fact that homolytic dissociation of the S-S bond in **1** occurs orders of magnitude more readily than homolytic dissociation of the S-S bond in an aryl disulfide,

ArSSAr. Thus, 2,2'-dibenzothiazolyl disulfide, which apparently undergoes homolysis much more readily than most aryl disulfides, still dissociates into radicals at a rate<sup>2</sup> only  $10^{-3}$  times that of *p*-tolyl *p*-toluenesulfinyl sulfone (**1a**, Ar = *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>), and experiments in this laboratory<sup>3</sup> indicate that the difference in the rates of homolytic dissociation of **1a** and *p*-tolyl disulfide is at least  $10^7$  at 100°. That merely changes in the oxidation state of the sulfur atoms participating in an S-S bond can lead to such profound changes in the ease of homolytic dissociation of that bond is most significant and would seem to be of great practical importance in sulfur chemistry. Before one can hope to know unequivocally the reasons for this behavior, one must have quantitative data on the ease of radical dissociation of the S-S bonds in all the other types of organic compounds containing a single sulfur-sulfur bond,

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