Dipolar Micelles. 6. Catalytic Effects of Betaine-Like Micelles on the Hydrolysis of Substituted Phenyl Esters

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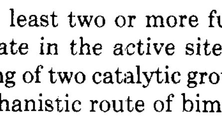
The catalytic effects of five betaine-like micelles on the hydrolysis of substituted phenyl esters were measured. The micellaric catalysts are of the general structure $[CH_3(CH_2)_nN^+(CH_3)_2(CH_2)_mCOOH]Br^-$, where $n = 9$, $m = 1$ (I); $n = 15$, $m = 1$ (IA); $n = 9$, $m = 2$ (II); $n = 9$, $m = 3$ (III); and $n = 15$, $m = 3$ (IIIA); compound IV, $n = 0$, $m = 1$, is also included in this study for comparison purposes. The following esters were examined: 2,4-dinitrophenyl acetate (OPNA); 2,4-dinitrophenyl hexanoate (OPNH); 2,4-dinitrophenyl decanoate (OPND); 4-nitrophenyl decanoate (PND); 3-nitrophenyl decanoate (MND); 2,5-dinitrophenyl decanoate (OMND). The catalytic rate constants (k_n) and the nucleophilic catalysis by hydroxide ion (k_{OH}) were determined. From the pH–rate profiles of OPNH in I and in IV, it is observed that in spite of the similarities in the pK_a values of I and IV the catalytic reactivity of the latter is inferior to that of I. Therefore, it is possible to conclude that the catalytic efficiency of I stems from the micelle–substrate intracomplex reaction, which is not the case in IV. The isotope effect of 1.1 determined for OPND in micelle I indicates that catalysis occurs via nucleophilic attack by the carboxylate anion. The plot of log k_{OH} against log k_n in micelle III for esters possessing various leaving groups is nonlinear. Esters having good leaving groups, as in OMND and OPND, fall on a line of slope 1, and the value of the deuterium isotope effect $[k_n(H_2O)/k_n(D_2O)]$ equals 1.15. On the other hand, for esters bearing poor leaving groups, as in MND and PND, the respective values of the slope and the deuterium solvent isotope effect are 2.2 and 1.95. Therefore, it is suggested that in micelle III the catalytic hydrolysis of OMND and OPND follows the nucleophilic route, whereas that of MND and PND approaches the general-base type route.

The participation of the carboxyl group in the catalytic route of proteolytic enzymes[1] has prompted many studies on monofunctional intramolecular catalysis as model systems.[2-10] Since at least two or more functional groups are known to participate in the active site of enzymes, chemical models consisting of two catalytic groups were tested.[11-14] As regards the mechanistic route of bimolecular[15] and intramolecular[5] catalysis of the carboxylate anion in phenyl acetate esters, Bruice and Benkavic[8c] concluded that a change in the mechanistic pathway from general base catalysis to nucleophilic catalysis occurs on the conversion of a bimolecular reaction to its intramolecular counterpart. This conclusion was also established in many other monoaryl esters of dicarboxylic acids.

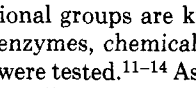
The enhancement of nucleophilic catalysis in intramolecular systems is attributed to the propinquity effect.

With regard to the mechanistic route of the carboxylate anion in intramolecular systems, an additional factor has to be considered. Fresht and Kirby[4b] have shown that the hydrolysis of aspirin anion proceeds via general base catalysis and changes to a nucleophilic mechanism in the case of 3,5-dinitroaspirin.[4c] The proposed borderline for maintaining a nucleophilic pathway requires that the leaving group is at most 2–3 pK_a units more basic than the carboxylate anion. A similar stiuation also exists in the intermolecular-catalyzed reaction of the ion on substituted phenyl acetates.[16]

Since the reaction occurring in catalytic micelles resembles that of a unimolecular process due to the intracomplex formation of substrate–micelle, the participation of the carboxylate group in the hydrolytic pathway might shed light on other parameters affecting either the catalyst or the substrate. Therefore, we designed five types of micelle-forming agents, I, IA, II, III, and IIIA, in an attempt to elucidate microenvironmental and proximity effects in the intramolecular catalysis of these systems.


$CH_3-\overset{CH_2COOH}{\underset{(CH_2)_nCH_3}{N^+}}-CH_3\ Br^-$

I, $n = 9$
IA, $n = 15$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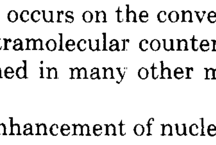
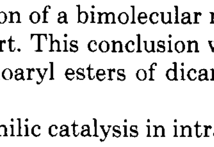
II


$CH_3-\overset{(CH_2)_3COOH}{\underset{(CH_2)_nCH_3}{N^+}}-CH_3\ Br^-$

III, $n = 9$
IIIA, $n = 15$


$CH_3-\overset{CH_2COOH}{\underset{CH_3}{N^+}}-CH_3\ Br^-$

IV

Catalytic micelles composed of carboxylic head groups might also serve as models for the bifunctional-catalyzed reaction since the internal pK_a value of the acidic species changes with an increasing amount of the dissociated[17] form.

Experimental Section

Reagents. All the micelle-forming agents have been described previously.[18a,b] The esters 2,4-dinitrophenyl acetate (OPNA), 2,4-dinitrophenyl hexanoate (OPNH), 2,4-dinitrophenyl decanoate (OPND), 2,5-dinitrophenyl decanoate (OMND), 4-nitrophenyl decanoate (PND), and 3-nitrophenyl decanoate (MND) were prepared and purified prior to use. The ester 2,4-dinitrophenyl hexanoate was prepared from hexanoyl chloride and 2,4-dinitrophenol in a solution of toluene followed by standard procedure. Anal. Calcd for $C_{12}H_{14}N_2O_6$: C, 51.06; H, 4.96; N, 9.92. Found: C, 51.35; H, 5.10; N, 10.09.

pH Measurements. The pH of the solution used in kinetics studies was measured by a Radiometer Model 26 pH meter with a GK-23226 combined glass electrode. The pH meter was calibrated with two buffer solutions of pH 1.67 and 6.47.

pK_a Measurements. A Radiometer titration assembly was used for the titration cell. Thermostated water at 30 °C was circulated through the jacketed cell. The detergent solution (0.1 M) was titrated with sodium hydroxide, and pK_a values for the various ionization states were found from the plot of $[pH - \log[\alpha/(1-\alpha)]]$ vs. α, where α is the degree of ionization. All pK_a values used in the discussion and in Figure 5 are those of the half-neutralization point ($\alpha = 0.5$).

Kinetic Studies. All kinetic measurements were performed in 0.1 M detergents at an ionic strength of 0.8 M or 2.5 M KCl and at a temperature of 30 or 60 °C on a Gilford 2000 spectrophotometer. Stock solutions of esters were prepared in acetonitrile (0.015 M). The reaction was initiated by the injection of 20 μL of the esters into a preequilibrated solution of micelles. The appearance of absorbance was followed at 328, 285, 350, and 330 nm for 2,4-dinitrophenol, 2,5-dinitrophenol, 4-nitrophenol, and 3-nitrophenol, respectively. The buffers used were valeric acid (0.015 M), succinic acid (0.015 M), and phosphate (0.03 M) in the pH ranges 3.5–5, 5–6, and 6–7.5, re-

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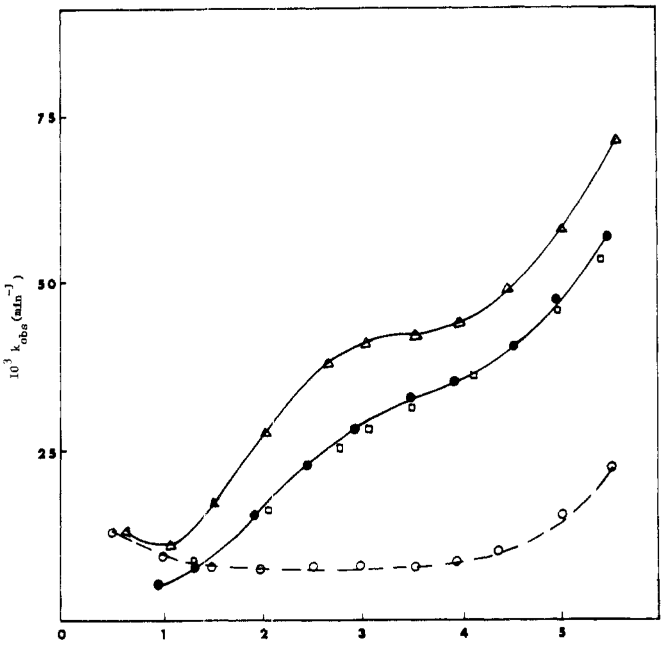

Figure 1. pH vs. k_{obsd} profiles for the hydrolysis of esters OPNA (-△-), OPNH (-●-), and OPND (-□-) in the presence of 0.1 M micelle I and OPNH (--○) in the presence of 0.1 M compound IV at 60 °C, μ = 0.8 M (KCl).

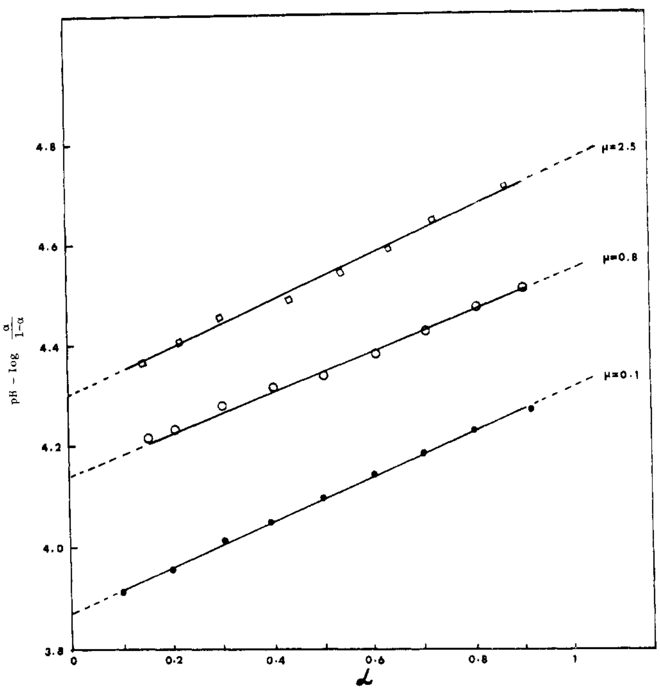

Figure 2. The variation of the intrinsic pK_a [pH − log [α/(1 − α)] with the degree of dissociation (α) for 0.1 M micelle III at 30 °C.

Table I. Hydrolytic Rate Constants[a] for 2,4-Dinitrophenyl Esters in 0.1 M Micelle I and in 0.1 M Compound IV

Catalyst; Rate constant	Esters OPNA	OPNH	OPND
I; $10^3 k_n$, min^{-1}	42	27	27
I; k_{OH}, min^{-1} M^{-1}	20 343	6850	8600
IV; $10^3 k_2$, min^{-1} M^{-1}	26	10	
IV; $10^3 k_0$, min^{-1}	10.7	4.5	
IV; k_{OH}, min^{-1}	45 000	28 000	

[a] Determined at 60 °C, μ = 0.8 M (KCl).

spectively. At pH's close to the pK_a of the micelles, the reactions were also carried out without any external buffers. In each case it was found that (a) on extrapolating the rate constants to zero buffer concentration the rate constants were identical with those obtained in the absence of a buffer and (b) the contribution of the buffers at the above-mentioned concentrations to the kinetic rate was not more than 2.5%.

The first-order rate constants of the micellar catalytic reaction were determined from the pH–rate constant profile (see Results and Discussion). The rate constants of the specific-base-catalyzed hydrolysis were determined using a phosphate or carbonate buffer in the pH range 7–8 or 9.5–10.5, respectively. From a linear plot of the first-order rate constant vs. the hydroxide ion concentration, the second-order rate constant (k_{OH}) can be calculated.

Results and Discussion

Figure 1 shows the pH–rate constant profiles for the esters OPNA, OPNH, and OPND in micelle I and for OPNH in IV. The rate constants of the catalytic group in micelle I (k_n) were determined from the plateau region of the pH–rate constant profile plots, where the contribution of the specific-base-catalyzed hydrolysis (k_{OH}) to the overall rate constant is negligible.

With compound IV as a catalyst, a broad low plateau is observed at 0.1 M, which is slightly dependent on the catalyst concentration. The plots of the first-order rate constants vs. the concentration of IV at pH 3.1 allows the second-order rate constant (k_2) and the spontaneous rate (k_0) to be determined.

From Figure 1 and Table I it is apparent that, in the hydrolysis of esters, the carboxylate anion in betaine catalyst IV and betaine-like catalyst micelle I operate by different mechanistic routes. This observation is unexpected since the pK_a values of the carboxylic group in I and IV are similar, and thus the groups should have a similar nucleophilic capacity (I, pK_a 2.20, and IV, pK_a 2.02, at 30 °C, μ = 0.8 M). The difference between the pK_a value of the nucleophile in IV and the leaving group in OPNH is in the range of 2–3 pK_a units, which is the proposed limit to maintain a nucleophilic catalysis. Therefore, in contrast to catalyst IV, it seems that the catalytic efficiency of I originates from the participation of the carboxylate anion in the substrate–micelle intracomplex reaction.

The suppressed nucleophilic reactivity of catalyst IV can be explained on the basis of strong electrostatic stabilization in the ground state as compared to the transition state. This is not the case in micellar intramolecular nucleophilic catalysis. In our previous studies,[18a,b] it was suggested that micelle I resembles an anionic micelle more than a cationic or uncharged micelle because of the strong binding of the negatively charged counterions to the surface. In analogy to other cationic micelles, it is assumed that at the experimental ionic strength of 0.8 M (KCl) 70–80% of the positively charged surface is neutralized.[20,21] The carboxylate anion therefore is less stabilized in the ground state and might react in nucleophilic displacements.

Furthermore, additional factors might also be responsible for the enhanced nucleophilic catalysis in micelle I. (a) Steric effects are assumed to orient both the reaction site and the attacking carboxylate anion to close proximity. The striking similarity in the hydrolytic rate of OPND and OPNH (Figure 1) points to the particular part played by the hydrophobic interactions bearing on the rate of hydrolysis.[18c] (b) From Figure 2 it can be inferred that the intrinsic pK_a value of micelle III increases by 0.3–0.7 unit as the dissociation of the acid is completed. Consequently, the nucleophilic efficiency of the carboxylate anion also increases. This phenomenon consti-

Table II. Rate Constants of OPND in 0.1 M Micelle I, II, and III

Micelle	Registry no.	Temp, °C	μ (KCl), M	pK_a	10^3k_n, min^{-1}	k_{OH}, min^{-1} M^{-1}
I	39995-54-5	30	2.5	2.66	2.5	590
		60	0.8	2.20	27 (24.5)[a]	8600
IA	5466-51-3	60	0.8	2.70	82	
II	26543-24-8	30	2.5	3.76	13	500
III	26851-20-1	30	2.5	4.56	60	480
		60	0.8	4.30	650 (565)[a]	30000
IIIA	64252-74-0	60	0.8	4.53	1000	

[a] Determined in D_2O.

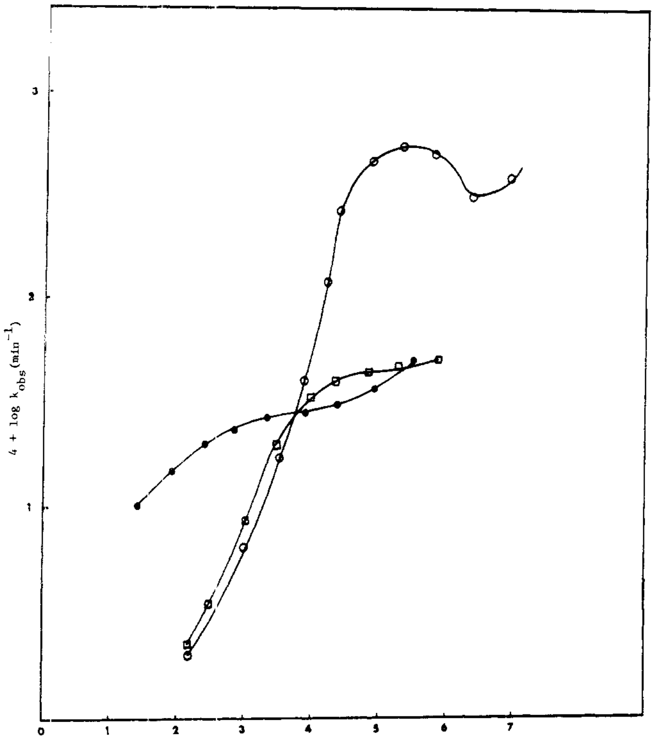

Figure 3. log k_{obsd} vs. pH profile for the hydrolysis of OPND in 0.1 M micelle I (-●-), II (-□-), and III (-○-) at 30 °C, μ = 2.5 M.

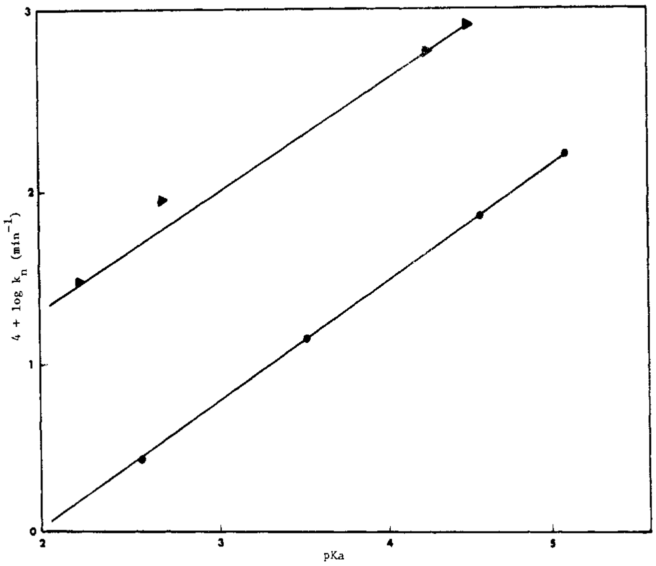

Figure 4. log k_n vs. pK_a of micelles I, II, and III in the hydrolysis of OPND (-●-) at 30 °C, μ = 2.5 M (KCl); (-▲-) at 60 °C, μ = 0.8 M (KCl).

tutes part of a more general microenvironmental effect which is one of the major factors of micellar reactivity.

Supporting evidence for the nucleophilic catalysis route in the hydrolysis of 2,4-dinitrophenyl esters with micelle I as a catalyst is also proven by the deuterium isotope effect. The experimental value of $k_n(H_2O)/k_n(D_2O)$ = 1.1 (Table II), determined for the hydrolysis of OPND, is in accord with this suggestion. Thus, it seems likely that in the presence of a more basic anion, such as in compounds II and III, a nucleophilic mechanism prevails.

Indeed, from the data represented in Table II and in Figure 3 it is apparent that the carboxylate anions of II and III participate in the hydrolysis of OPND, and the enhancing effect is also reflected by the increased pK_a values of the nucleophiles. Moreover, the kinetic isotope effect of 1.15 as observed in micelle III supports this view. Interestingly, it was noted that the reaction of OPND in micelles I, IA, II, III, and IIIA provides a linear Brønsted correlation with the basicity of the carboxylate residue (see Figure 4). The β values of 0.7 and 0.75, obtained from the plots in Figure 3, are in accord with other reported β values for intramolecular nucleophilic reactions of carboxylate anions in substituted phenyl succinates, phenyl glutarates,[15,14a] and phthalate esters[8f] (i.e., β = 0.8–1.14). This latter range of β values was observed also in other systems of nucleophilic reactions, where the leaving group and the attacking nucleophile are of similar basicity.[16,22] It is well-known that a change in the degree of ionization of a micellized head group affects the hydrophilic–lipophilic balance of micelles. Consequently, the question asked is if one can draw a conclusion from the β value attributed to the pK_a of half-neutralization on the reaction pathway. However, in the betaine series it was found that the slope of the linear relationship [pH − log [$\alpha/(1-\alpha)$]] vs. α for micelle III at 30 °C, μ = 0.8 M, is very similar to that of micelle I measured under the same conditions. The corresponding values are 0.42 and 0.48. This fact indicates that in the betaine micelles the Brønsted β value is almost independent of the extent of ionization. Thus, we are inclined to accept the possibility that in analogy to nonmicellar systems the β coefficient, as obtained in the betaine-like micelles, is an additional criterion for a nucleophilic route. Moreover, additional results (Figure 5) indicate that as the basicity of the ester leaving group increases the hydrolytic pathway changes to an intramolecular general base catalysis. Inspection of Figure 5 reveals that on plotting log k_n vs. log k_{OH} for OPND, OMND, PND, and MND in micelle III the points are not linearly correlated. The esters possessing good leaving groups (OPND and OMND) fall on a line of slope 1, while the esters PND and MND lie on a line of slope 2.2. That such a phenomenon might reflect a change in reaction mechanism is well-known in analogous systems.[16,23,24] Furthermore, it was experimentally found that the deuterium isotope effect [$k_n(H_2O)/k_n(D_2O)$] of PND in micelle III is 1.95. Thus, it seems likely that, whereas the esters OPND and OMND are hydrolyzed via a nucleophilic mechanism, the

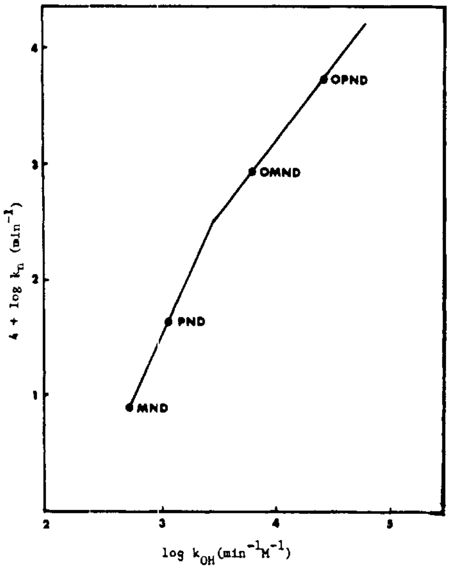

Figure 5. log k_n vs. log k_{OH} for substituted phenyl decanoate esters in 0.1 M micelle III at 60 °C, μ = 0.8 M (KCl).

hydrolytic pathway of PND and MND approaches a general base catalysis.

The latter results are unexpected since it is known that carboxylate anion will react as an intramolecular nucleophile even if the difference in pK_a between the attacking and leaving groups is large (ΔpK_a = 5–6 units). This is in marked contrast to the corresponding intermolecular systems where a ΔpK_a of 2–3 units might change the mechanism to general base catalysis. Since the hydrolysis of PND in the presence of micelle III was interpreted as indicating general base catalysis, it seems likely that the efficiency of the carboxylate anion in a micellar system closely resembles an intermolecular catalysis. (The pK_a of p-nitrophenol at 25 °C and that of micelle III at 30 °C is 7.2 and 4.3, respectively.) On the other hand, the above-mentioned results (Figure 1, compounds I and IV) indicate that betaine-like micelle I is a better nucleophile than betaine IV, due to the ability of I to react in an intramicellar pathway. Therefore, it can be assumed that, when compared to an intermolecular reaction, the carboxylate anion in a micellar system is probably a more efficient catalyst, but much less efficient than in other intramolecular reactions.

In order to gain more kinetic information on the catalytic potency of the carboxylate anion in micellar and other intramolecular systems, it is necessary to compare systems bearing both identical leaving groups and carboxylic groups of equal basicity. Because of this limitation, we estimated the rate constant of a model derived from mono-2,5-dinitrophenyl glutarate, where the pK_a value of the free carboxylic group is that of compound III. On using the data of Bruice and Pandit[8b] for the hydrolysis of mono-p-bromophenyl glutarate, and considering a Brønsted β coefficient of 1.14 for the leaving groups and 0.8 for the carboxylic nucleophile, it was found that the first-order rate constant of mono-2,5-dinitrophenyl glutarate, possessing a carboxylic group of pK_a = 4.3, is 238 min^{-1} at 30 °C. On the other hand, the pseudo-first-order rate constant of OPNA in 0.1 M acetate is 0.0033 min^{-1}. (The second-order rate constant of OPNA with acetate anion is 0.032–0.034 min^{-1} M^{-1} at 25 °C.[16,25]) These kinetic results conform with the view of an intermediate role of the carboxylate anion in a micellar system. The carboxylate anion in micelle III is 238/0.06 $\simeq$ 4000 times less reactive than the corresponding carboxylate anion in an intramolecular system of glutaric acid monoester, but 0.06/0.0033 $\simeq$ 18 times more reactive than the acetate ion in a bimolecular reaction.

It is noteworthy that, in contrast to other intramolecular systems, the capability of the carboxylate anion in micelles to participate in hydrolytic reactions is restricted. It was experimentally observed that the rate constant of PNA hydrolysis in micelle I is 0.0025 min^{-1} (μ = 0.8 M, 80 °C). The latter value was also found for the hydrolysis of PNA in the absence of catalyst I. However, on replacing micelle I (pK_a = 2.25 at 80 °C, μ = 0.8 M) by micelle IA (pK_1 = 2.45 at 80 °C, μ = 0.8 M), the first-order rate constant increased to a value of 0.0043 min^{-1}. These results indicate that in the case of micelle I a ΔpK_a of 5 units between the leaving group of the ester and the carboxylic group of the micelle is the upper limit for catalysis.

Although carboxylic micelles exhibit a low catalytic potency, the system is of general interest due to its ability to affect reactions in an analogous way to polyelectrolytes and to induce various microenvironmental effects in the vicinity of the reaction site.

Inspection of Table II reveals that the specific base catalysis reaction in the presence of micelles I, II, and III is strongly dependent on the ionic strength of the solution. Whereas at an ionic strength of 0.8 M micelle I inhibits the reaction rate as compared to micelle III, at an ionic strength of 2.5 M the reaction rates in the presence of the three micelles are similar. However, the relative catalytic power of the above micelles is not effected by a change in the ionic strength. This suggests that the carboxylic head groups of micelles I, II, and III reside in similar regions in the vicinity of the surface and are exposed to the same degree of electrostatic interactions. Consequently, the folded conformation seems to be the preferred state of the alkyl head group in micelles II and III.

An interesting phenomenon can be noticed in Figure 3. The pH–rate profile of OPND in micelle III exhibited a bell-shaped curve in the pH range of 4.5–6.5. From potentiometric measurements of polymeric acids and bases, it is known that the intrinsic dissociation constant of the polyion is dependent on its degree of ionization.[17] Similar behavior was observed in micelle III (Figure 2). At first glance it seems that the kinetic bell shape might be derived from a bifunctional catalysis due to the change of the pK_a value at various degrees of ionization, but the small difference of 0.5 unit in ΔpK_a does not support this suggestion. Moreover, in experiments aimed to detect bifunctional catalysis in a mixed micelle system (I + III, 1:1), no evidence for this pathway could be obtained. The possibility that the bell shape is derived from electrostatic effects operating on the specific base catalysis can also be excluded: (a) the contribution of specific base catalysis at a pH range of 4.5–6.5 is very small as compared to the catalytic rate of the carboxylate anion; (b) at higher temperatures, where the rate of the specific base catalysis is increased, the bell shape is less pronounced.

A reasonable explanation for the bell-shaped pH–rate profile can be given on the basis of the reverse reaction in which the phenoxide ion of the leaving group attacks the anhydride formed during the reaction. Therefore, it can be assumed that (a) the diffusion of the leaving group from the Stern layer should be slow, (b) the phenoxide ion should reside in close proximity to the anhydride intermediate, and (c) the pK_a value of the phenoxide ion should be greater than that of the micellar carboxylic group. Indeed, further observations indicate that the reverse reaction is favorable.

On adding 8.5 × 10^{-4} M 2,4-dinitrophenol to the reaction mixture, which consisted of OPND in micelle III, the first-order rate constant was reduced. Moreover, at pH 6.4 (peak), the rate constant was decreased by 2.2-fold and at pH 5.4 (trough) by 1.3-fold. These results are in accord with the assumed reversibility of the reaction and might account for the bell shape in Figure 3.

A further study is in progress.[21]

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Registry No.—IV, 5938-06-7; OPNA, 4232-27-3; OPNH, 64252-81-9; OPND, 61063-34-1; OMND, 61063-35-2; PND, 1956-09-8; MND, 61063-38-5; hexanoyl chloride, 142-61-0; 2,4-dinitrophenol, 51-28-5.

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(18) (a) Part 3: Rina Schiffman, M. Chevion, Ch. Rav-Acha, J. Katzhendler, and S. Sarel, *J. Org. Chem.*, **42,** 856 (1977); (b) Part 4 and 5: sent for publication. (c) The OPNH ester is assumed to be almost fully incorporated into the micelle. This is based on the association constant (*K*) which was kinetically determined for the esters *p*-nitrophenyl hexanoate, *p*-nitrophenyl acetate and OPNA in a cholinium micelle (see ref 18a). The corresponding *K*/*N* values are 102, 19, and 13 (*N* denotes the aggregation number, ~40.
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Syntheses of Electronegative Substituted Tetrathiafulvalene Derivatives

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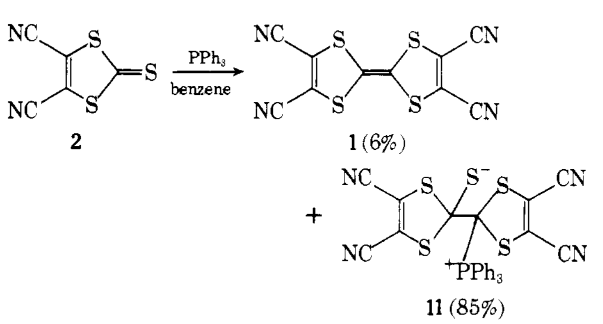
Tetracyano-, tetracarbomethoxy-, and tetraphenyltetrathiafulvalene have been prepared from 4,5-disubstituted 1,3-dithiole-2-thiones in the presence of triphenylphosphine and trialkyl and triphenyl phosphites. Acid- and base-catalyzed hydrolyses of tetracyano- and tetracarbomethoxytetrathiafulvalenes led to the formation of new derivatives. A new synthetic route to parent tetrathiafulvalene was established.

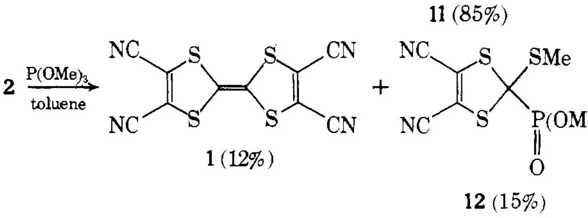
The phenomenon of high electrical conductivity[1] in the complex of tetrathiafulvalene (TTF) with tetracyanoquinodimethane (TCNQ) has recently aroused intense interests. Several synthetic methods[2] of TTF derivatives have been reported so far: (i) deprotonation of 1,3-dithiolium ions;[3] (ii) desulfurization of 1,3-dithiole-2-thiones with trivalent phosphorus compounds;[4] (iii) pyrolysis of orthothiooxalates;[5] (iv) reaction of acetylenes with carbon disulfide.[6,4b] As a series of our study[4f,7,8] on the reactions of thiocarbonyl compounds with trialkyl phosphites, we previously reported[4f] the successful synthesis of tetracyanotetrathiafulvalene (**1**) by the reaction of 4,5-dicyano-1,3-dithiole-2-thione (**2**) with triphenyl phosphite. In this paper, we wish to report the application of this synthetic method to the preparation of tetracarbomethoxytetrathiafulvalene (**3**) from 4,5-dicarbomethoxy-1,3-dithiole-2-thione (**4**) and tetraphenyltetrathiafulvalene (**5**) from 4,5-diphenyl-1,3-dithiole-2-thione (**6**). Tetracyano-,[4d-f] tetracarbomethoxy-,[4b,g] and tetraphenyltetrathiafulvalene[3b] have all been previously synthesized. By the acid hydrolyses of **1** and **3**, tetraamidetetrathiafulvalene (**7**) and dicarboxytetrathiafulvalene (**9**) were newly obtained, respectively. The alkaline hydrolysis of **3** led to the formation of tetracarboxytetrathiafulvalene (**8**), which was converted to its anhydride (**10**) and **9**. Pyrolysis of **9** provided a new synthetic route to parent tetrathiafulvalene in good yields.

Results and Discussion

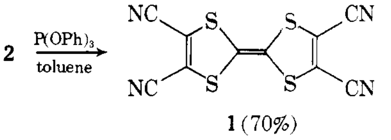
The synthesis of tetracyanotetrathiafulvalene (**1**) by the reactions of 4,5-dicyano-1,3-dithiole-2-thione (**2**) with triphenylphosphine, trialkyl, and triphenyl phosphite was briefly reported in our preceeding communication.[4f] The procedure in detail is described in the Experimental Section of this paper. In the reaction of **2** with triphenylphosphine in benzene under reflux, **1** was obtained only in 6% yield and the betaine



2 **1** (6%) + **11** (85%) (1)



2 → **1** (12%) + **12** (15%) (2)



2 → **1** (70%) (3)