Aggregation of Alkylammonium Carboxylates and Aerosol-OT in Apolar Solvents Studied Using Absorption and Fluorescence Probes

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Abstract: Using optical probes, the aggregation of 16 different alkylammonium (C_{10} to C_{14}) carboxylates (C_2 to C_{11}) has been investigated in dry benzene, cyclohexane, and carbon tetrachloride, as well as Aerosol-OT in benzene. At the very low concentrations of the absorption (acridine orange and iodine) and fluorescence probes used (octyl-, dodecyl-, and tetradecylammonium 8-anilino-1-naphthalenesulfonates), only the iodine probe had a significant effect on the aggregation of the surfactant. Critical micelle concentrations were determined by the Corrin–Harkins method, and in a few cases aggregation numbers and association constants were calculated by Adams' method using vapor pressure osmometric results. For the alkylammonium carboxylates the onset of aggregation is gradual, leading to small aggregates (average aggregation number $\bar{n} \approx 3$) with the monomer population and $\bar{n}$ dependent on the concentration. In these systems the concept of cmc is used only in an operational sense. For Aerosol-OT the onset of micelle formation is sharper, leading to larger aggregates ($\bar{n} \approx 10$) with the monomer population and aggregation number independent of the concentration. The effects of the solvent, the nature of the probe, and the length of the alkylammonium and counterion chains on the aggregation tendency are discussed.

Introduction

In recent years there has been an increasing interest in structured aggregates of amphiphilic molecules in nonpolar solvents, mainly because of their practical applications as catalysts[2] and solubilizing agents,[3] as well as for their suitability as model systems for membranes[4] and for stepwise association in general.

Aggregation is usually recognized by changes in the colligative properties of a system, or by the use of probes (such as NMR,[5] water[6] or dye[7] solubilization, etc.). Probes, in general, are species with some characteristic physical property that can be monitored experimentally at such sensitivity level that changes in the interaction between the probe and the system under investigation can be detected and interpreted as meaningful information. One expects the presence of an ideal probe not to significantly perturb the system it is to measure.

The present study was undertaken to investigate the suitability of optical probes to detect aggregation. Such probes would facilitate the study of both the static and dynamic properties of systems of amphiphilic molecules. The rate processes involved in aggregation and micelle formation are very fast and usually specialized (relaxation) techniques have to be used for their measurement, where optical detection is the one most commonly used.

We report the successful use of absorption (acridine orange base AO and iodine) and fluorescence probes (octyl-, dodecyl-, and tetradecylammonium 8-anilino-1-naphthalenesulfonates, with the symbols OA-ANS, DA-ANS, and TA-ANS, respectively) in the detection of the aggregation of 16 different alkylammonium carboxylates in pure benzene, cyclohexane, and carbon tetrachloride, as well as of Aerosol-OT [di-(2-ethylhexyl)sodium sulfosuccinate] in benzene at 25 °C. The effect of the presence of the probes on the cmc and the aggregation numbers (as determined using vapor pressure osmometry) is discussed.

Experimental Section

Chemicals. The *solvents* benzene and cyclohexane were dried and distilled over sodium, and carbon tetrachloride over P_2O_5. Even with such careful drying procedures, the water content of the solvents was found to be 0.03% by weight as determined by the Karl Fischer method. The *surfactants* tetradecylammonium, dodecylammonium, and decylammonium carboxylate were prepared as described in the literature.[5] They were recrystallized three times from *n*-hexane and stored in vacuo over P_2O_5. Aerosol-OT (Dow Chemical Co.) was purified according to the method given in ref 8.

Probes. The AO base was obtained by treating a 10^{-3} M aqueous acridine orange (Eastman Kodak Co.) solution with 6 N NaOH. The free base was extracted with benzene, which after drying and evaporation of the solvent remained. Sublimed iodine (Baker analyzed reagent) was used without purification. The fluorescence probes OA-ANS, DA-ANS, and TA-ANS were prepared from 8-anilino-1-naphthalenesulfonic acid (Eastman Kodak Co.) and from the corresponding freshly distilled alkylamines (Aldrich Chemical Co.). In each case 30 mmol of the acid and 30 mmol of the amine were refluxed for 5 h in 60 mL of dried benzene. After partial evaporation to a volume of ca. 30 mL the products precipitated. The light yellow substances were recrystallized three times from *n*-hexane and stored in vacuo above P_2O_5.

All probes are well soluble in benzene; however, because of its higher polarity, OA-ANS is nearly insoluble in cyclohexane. Therefore, OA-ANS was not used as a probe in that solvent.

Absorption Measurements. The visible absorption spectra were recorded on a Cary 14 spectrophotometer at 25 °C using 1-cm path length cells. The pure AO benzene solutions have only one prominent absorption band at 425 nm which does not obey the Bouguer–Lambert–Beer law. With increasing concentration the dye shows a hypochromic effect: on an eightfold concentration increase from 5×10^{-6} to 4×10^{-5} M, the molar decadic extinction coefficient ϵ_{425} increases from 8.9×10^2 only to 5.35×10^3 M^{-1} cm^{-1}, respectively. The spectrum shape and the location of the absorption band stay unchanged.

AO was used as a probe at a concentration of 2×10^{-5} M (4×10^{-5} M in case of Aerosol-OT) in surfactant solutions of the concentration ranging from 1×10^{-4} to 3×10^{-2} M. The presence of surfactants causes the appearance of a new absorption band at 490 nm, and the original absorption band is red shifted to 430 nm (e.g., Figure 1).

If the apparent molar extinction coefficient of the surfactant–AO solutions ϵ ($\approx A(\text{path length})^{-1}(\text{surfactant concentration})^{-1}$) is plotted vs. the surfactant concentration (as it is done in the Corrin–Harkins method[9] of determination of the critical micelle concentration, cmc) one obtains Figure 2. The intersection of the tangents of the linear portions of the curves is traditionally interpreted as the cmc of the particular surfactant. This method was used as a test for the functioning of the probes.

At this point it should be emphasized that the conventional concept of the cmc, as it is used in aqueous solutions, is not generally transferable to all aggregations of amphiphilic molecules in dry, nonpolar solvents.[10] In apolar solvents the onset of the formation of larger aggregates is often unsharp, and the average aggregation number, as well as the monomer concentration, may be functions of the total surfactant concentration. Thus, the designation reversed or inverted

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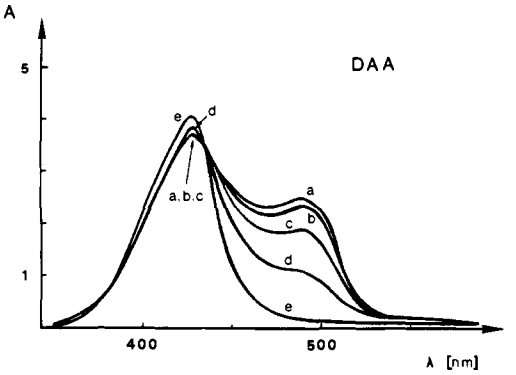

Figure 1. Absorption spectrum of dodecylammonium acetate (DAA) with AO probe (2×10^{-5} M) in benzene at 25 °C. The intensity of the new absorption band at 490 nm is a function of the DAA concentration: (a) 3×10^{-3} M; (b) 1.5×10^{-3} M; (c) 1×10^{-3} M; (d) 5×10^{-4} M; (e) zero (pure AO solution).

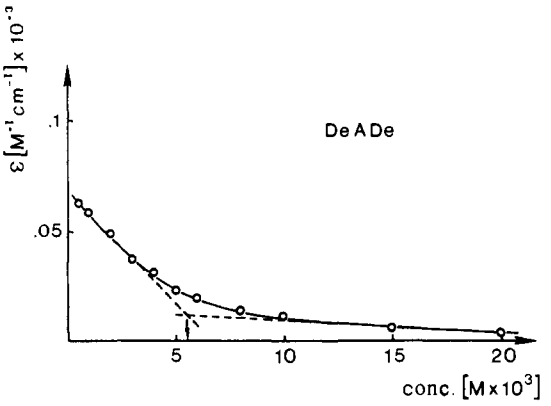

Figure 2. Apparent molar extinction coefficient ε of decylammonium decanoate (DeADe) with AO (2×10^{-5} M) in benzene at 25 °C and λ 490 nm vs. the concentration of DeADe. Example for the Corrin-Harkins method.[9]

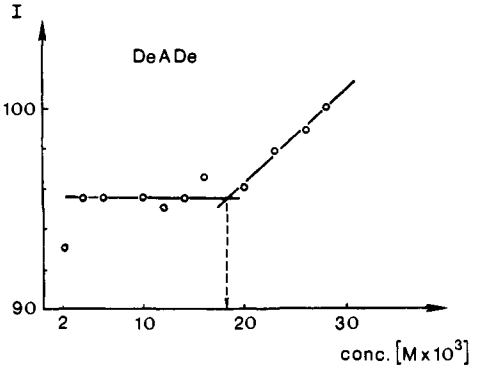

Figure 3. Fluorescence intensity I (in arbitrary units) of OA-ANS (5×10^{-6} M) vs. surfactant concentration of DeADe in benzene at 25 °C.

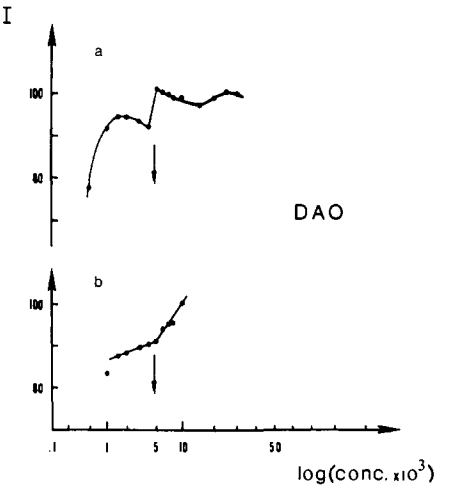

Figure 4. Comparison of the fluorescence intensity I (in arbitrary units) vs. log surfactant concentration plots for DAO as affected by the alkyl chain length of the probe: (a) equal chain lengths of DAO and the probe DA-ANS (5×10^{-7} M); (b) the alkyl chain of the probe OA-ANS (5×10^{-6} M) is shorter than that of the surfactant DAO.

micelle should only be used with qualification. In the present paper the concept of cmc is used in an *operational sense*, as a characteristic point rendering a basis for comparison of methods for detecting the progress of aggregation.

Table I summarizes the results obtained. In cases (DAP, DAB, and Aerosol-OT) where data has been available for comparison, the agreement is good. This indicates that the probe does not significantly affect the micellization, and it senses the same aggregation process that are detected by NMR,[5,11] conductance,[12] etc. Further discussion of the effect of the presence of AO is given in subsequent sections where a comparison is made with the fluorescence probes. At AO concentrations higher than 5×10^{-5} M the cmc decreases, similarly to the behavior of micelle systems in aqueous solution.[13]

Fluorescence Measurements. The fluorescence intensity measurements were done on a Perkin-Elmer fluorescence spectrophotometer 204 at 25 °C, at the wavelength of maximum emission of the pure probe solutions. For all our probes (OA-ANS, DA-ANS, and TA-ANS) in surfactant solutions, the indicator concentration was kept between 7×10^{-7} and 5×10^{-6} M. The intensity measurements were done at the fluorescence maximum of the dyes (λ 465 nm in carbon tetrachloride and benzene, and λ 450 nm in cyclohexane), with the excitation in benzene and CCl_4 at λ 375 nm, and at λ 385 nm in cyclohexane.

If the fluorescence intensity (in arbitrary units) is plotted vs. the surfactant concentration, again, the intersection of the linear portions of the curves can be designated as the operational cmc. The results are, within the experimental error, identical with those obtained from semilogarithmic plots. Figure 3 shows a typical curve, and Table II summarizes the results obtained in benzene, cyclohexane, and carbon tetrachloride at 25 °C.

Typically, the fluorescence intensity, I, increases in the presence of surfactants. As the surfactant concentration is increased, I rises first, then remains nearly constant. Then I increases again at the cmc. Fluorescence behavior of the type depicted in Figure 3 is exhibited by a system only if the alkyl chain of the probe is shorter than the alkyl chain of the amine of the surfactant, e.g., DA-ANS is suitable for the tetradecylammonium carboxylates. Otherwise, the concentration dependence of the fluorescence intensity cannot be approximated by intersecting linear portions. Nevertheless, in these cases a pronounced break is found in the concentration range of the cmc[15] (Figure 4).

Vapor Pressure Osmometry. In order to test the influence of the absorption probe on the average aggregation number of the surfactants, osmometric measurements were carried out on DAP in the presence of AO, as well as on TAH, DAP, DAO, and Aerosol-OT without the indicator. Vapor pressure osmometry is the most advantageous and accurate technique to determine the average size of small aggregates (mol wt $<6 \times 10^3$), and it has recently been used to study association in nonpolar solvents.[11]

A Hewlett-Packard Model 302B vapor pressure osmometer equipped with a temperature controller for 37 °C was used in the measurements. Recrystallized benzil served for calibrating the instrument, according to the manufacturer's instructions. With the benzil calibrations, a steady state was obtained in 1 min; experimental readings were taken after 2 min.

The average aggregation numbers $\bar{n}$ were obtained by the method given by Adams et al.[11] The results are listed in Table I. For the alkylammonium carboxylates, the aggregation number steadily increases with the concentration in the range of 3×10^{-3} to 70×10^{-3} M. Our results are in full agreement with those given in ref 11. At the low probe concentrations we used, the presence of AO has no effect on $\bar{n}$ for DAP.

In the case of Aerosol-OT, investigated in the concentration range of 2×10^{-3} to 4×10^{-2} M, a concentration-independent constant $\bar{n} \approx 10$ was found. If five water molecules per Aerosol-OT are solubi-

Table I. Operational cmc Values Obtained with the Acridine Orange Probe (2×10^{-5} M) at 25 °C, Mean Aggregation Numbers, and Association Constants at 37 °C in Benzene

compd	symbol	cmc $\times 10^3$ M	lit. value of cmc $\times 10^3$ M	mean aggregation number[b] at 37 °C	K_i, M^{-1}, at 37°C
tetradecylammonium acetate	TAA	1.7			
propionate	TAP	1.4			
butyrate	TAB	1.6			
hexanoate	TAH	1.7		3	67.6
octanoate	TAO	2			
decanoate	TADe	2.5			
dodecylammonium acetate	DAA	3.5			
propionate	DAP	3.8 (2.3)[a]	3–7 (ref 5)	3 (3)[c] (3)[e]	69.5 (67.7)[c] (62.3)[e]
butyrate	DAB	3.5	3.8 (at 37 °C: ref 11)		
hexanoate	DAH	3			
octanoate	DAO	4.7		3	65.2
decanoate	DADe	3.8			
decylammonium acetate	DeAA	3.3			
propionate	DeAP	5			
octanoate	DeAO	5.5			
decanoate	DeADe	5.8			
Aerosol-OT	AOT	0.7	0.5 (ref 12)	10 (22)[d]	

[a] Using iodine as indicator (2×10^{-5} M). [b] At the cmc. [c] From ref 11. [d] From ref 6. [e] At an AO concentration of 2×10^{-5} M.

Table II. Operational cmc Values at 25 °C in Benzene and Cyclohexane Obtained with the Fluorescence Probes

	cmc $\times 10^3$ M in benzene			cmc $\times 10^3$ M in cyclohexane	
compd[a]	5×10^{-6} M OA-ANS	2×10^{-6} M DA-ANS	5×10^{-7} M TA-ANS	2×10^{-6} M OA-ANS	ref 7[c]
TAA		1.25	1.2		
TAP		1.3	1.2	0.28–0.32	
TAB		1.8	1.6	0.56–0.6	
TAH		1.7	2.2	1.4–1.6	
TAO		1.9	1.8	1.4	
TADe		2.12	1.5	1.2 –1.4	
TAD		2.2			
DAA	4.5–4.8	5			
DAP	5–5.5	4–7		1.56 (19 and 30)[b]	0.74–0.79
DAB	7	6		1.6	0.72–0.73
DAH	5.6–6	7		1.6–1.8	
DAO	5	5–8		2.1–2.5	0.89
DADe	9.6–10			2.2	1
DeAA	17				
DeAP	11–12			4	
DeAO	12–13				
DeADe	19–20			4.7–5	

[a] For symbols see Table I. [b] In CCl_4 with 3×10^{-5} M OA-ANS, there are two breaks in the fluorescence intensity vs. log surfactant concentration plot at 19 and 30 mM. These values are similar to those obtained by NMR: 21–25 mM (ref 14). [c] These data were obtained by the dye solubilization method. Since the solutions were saturated with the dye, its effect is a pronounced lowering of the cmc.

lized by the micelles, the average size of the aggregates increases to a constant $\bar{n} \approx 12$.

Discussion

The typical features of aqueous micelle systems, viz., the practically concentration-independent cmc and average aggregation number, are not generally characteristic of amphiphiles in nonpolar solvents. It seems that in dry, apolar solvents one has to distinguish at least two main, phenomenologically different types of aggregation of surfactants: (1) where the onset of association falls in a narrow concentration range at the cmc, leading to the formation of reversed micelles with constant average aggregation number (Aerosol-OT is a good example of such behavior); (2) where the onset of the association is less sharp than in the first case, spreading over a wider concentration range around the *operational cmc*, leading to the formation of aggregates with a concentration-dependent average aggregation number (the alkylammonium carboxylates are representative of this class). The optical probes we used accurately reflect these pictures.

Considering the interactions that contribute to the formation of aggregates, one has to account for dispersion forces between molecules of the solvent, between the hydrocarbon groups of the micelle and the solvent, as well as between the apolar groups of the monomers forming the micelle. Depending on the nature of the surfactant, repulsive and/or attractive electrostatic interactions are also present involving the polar or ionic head groups. Clearly, the subtle balance of the interactions together with steric effects determines whether the aggregation of a surfactant in a particular solvent is of type (1) or (2). Yet, if one accepts the definition that a micelle is any soluble aggregate (excluding vesicles) which is spontaneously and reversibly formed from amphiphilic molecules or ions,[16] both aggregations type (1) and (2) lead to micelle formation. The most pronounced differences between the two types of micelles are, perhaps, their shape and their population distri-

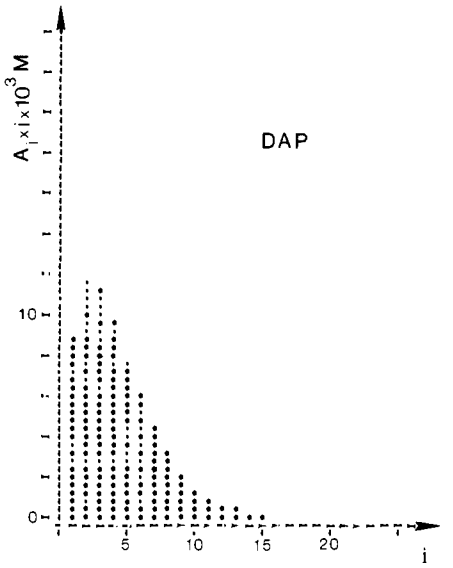

Figure 5. Example for the population distribution in aggregation space of alkylammonium carboxylates in benzene at 37 °C. The particular distribution is given for DAP at a concentration of 7.3×10^{-2} M. The population of the ith aggregate is given in millimoles of surfactant monomer per liter. The largest amount of the surfactant (~19%) is in the dimer ($i = 2$) form, and less than 0.5% is in the form of micelle with aggregation number $i = 15$.

bution in aggregation space. Type (1) micelles are usually spherical or ellipsoidal, and the type (2) ones are probably rod-like or lamellar, allowing for a continuous addition of monomers to the micelle at increasing surfactant concentration, with no geometrical restrictions to growth. At a concentration above the cmc, in type (1) systems only the monomer and the micelle states are populated to a significant extent, whereas in type (2) systems the population of small aggregates (oligomers) is more pronounced. Figure 5 shows an example of the latter case we computed for DAP, based on our vapor pressure osmometric results obtained in benzene at 37 °C, using Adams et al.'s method.[11] As our representative calculations for TAH, DAP, and DAO indicate the aggregation of the alkylammonium carboxylates can be best described by the "indefinite self-association with equal equilibrium constants (K_i)" model, as was already found for DAP.[11] In this model it is assumed that all associating species are present at significant concentrations, and all association constants K_i are equal. Our comparative computer calculations showed this model to be a clearly better description than the one obtained by Steiner's stepwise generation of consecutive association constants.[17] The equilibrium constants and aggregation numbers we calculated are listed in Table I, together with literature values, if available.

With regard to the micellization tendency of the alkylammonium carboxylates, as reflected in their operational cmc's (lower cmc indicating higher micellization tendency), the main influencing factors are (a) the solvent, (b) the chain length of the alkylamine, (c) the chain length of the counterion, and (d) the concentration and the nature of the probe. Based on the results summarized in Tables I and II, one can establish the following general trends.

(a) Where comparison is possible, the micellization tendency in the three solvents can be described as cyclohexane > benzene > carbon tetrachloride.

(b) Micellization is facilitated by the increasing length of the alkylammonium chain.

(c) Micellization is depressed by the increasing counterion chain length.

(d) With the acridine orange probe at concentrations higher than 5×10^{-5} M, the presence of the dye promotes micellization. However, at the low probe concentrations used (on the average 150 times below the cmc's), AO apparently has little effect on the onset of micellization in benzene. The much smaller iodine molecule, if used as a probe, promotes aggregation even at a concentration of 2×10^{-5} M. Its effect may be related to a charge-transfer equilibrium between probe and surfactant. In the case of DAP we calculated the common equilibrium constant K_i of the association steps in benzene, using vapor pressure osmometric data obtained both in the presence and absence of AO (Table I). The K_i's are lowered somewhat by the probe, slightly increasing the population of the oligomers.

The influence of the fluorescence probes is somewhat different. In the tetradecylammonium series, the indicators have apparently no effect on the aggregation (compare Tables I and II). In the dodecyl- and decylammonium series, the fluorescence probes lower the micellization tendency as compared with the effect of AO in benzene, or as compared with literature values[7] in cyclohexane. However, an advantage of the fluorescence probes may be that they are more sensitive than the absorption probe and hence they can be used at much lower concentrations (2×10^3 times below the cmc's) than AO. The alkyl chain length of the fluorescence probes affects only the appearance of the I vs. surfactant concentration plots, but not the value of the cmc (Figure 4).

In summary, one can rationalize the functioning of the optical probes by assuming that their polar part is incorporated in the polar interior of the aggregates when they are formed, and their nonpolar part is surrounded by the hydrophobic chains of the surfactant and/or by solvent molecules. The change of the microenvironment of the chromophores is reflected in the alteration of the absorption and fluorescence properties of the probes, irrespective of the sharpness of the onset of the aggregation and the size (aggregation number) of the micelles. The fact that also small aggregates (oligomers) are detected by the probes suggests that the *immediate* vicinity of the chromophores is responsible for the changes in their spectroscopic properties. As soon as the flat chromophore is interacting from one side with a surfactant monomer or a larger aggregate, its absorption and fluorescence properties start to change. When an interaction from the other side causes a further electronic perturbation of the chromophore, an additional and probably final change in the probe's spectroscopic properties takes place. (Thus, the probe sandwiched between two surfactant monomers, or incorporated in a larger aggregate, must have very similar spectroscopic properties.) The fine structure of the fluorescence curves (Figure 5) may be related to such a two-stage indication action. With increasing surfactant concentration, the probe-surfactant interaction equilibria are shifted toward complete solubilization of the dye by the aggregates, leading to the "saturation" of the sensing ability of the probe at the high surfactant concentration limit.

Owing to the low concentration of the indicators, only a small fraction of the aggregates is labeled by the probe molecules. Hence, in most cases the presence of the probes represents negligible influence on the aggregation.

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Ortho Ester Hydrolysis: Direct Evidence for a Three-Stage Reaction Mechanism

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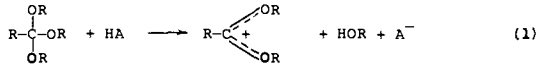
Abstract: Direct evidence is supplied for the existence of 1,3-dioxolenium ion and hydrogen ortho ester intermediates in the acid-catalyzed hydrolysis of a series of 2-aryl- (and 2-cyclopropyl-) 2-alkoxy-1,3-dioxolanes. These two intermediates require a three-stage reaction path: (1) loss of the exocyclic alkoxy group from the substrate to generate the dioxolenium ion, (2) reaction of this ion with water to form hydrogen ortho ester, and (3) breakdown of the hydrogen ortho ester to carboxylic acid products. Rate constants for all three stages and equilibrium constants for stage 2 were measured in some cases and were estimated in others. Differential substituent effects of phenyl and cyclopropyl on stages 1 and 3 are shown to be responsible for the changes in rate-determining step which these systems undergo between low (stage 3 rate determining) and high (stage 1 rate determining) pH. The purely aliphatic ortho esters 2-methoxy-1,3-dioxolane and 2-methyl-2-methoxy-1,3-dioxolane were found not to give this change in rate-determining step.

It is now generally accepted that the acid-catalyzed hydrolysis of ortho esters consists of three separate reaction stages: (1) generation of a dialkoxy carbonium ion, (2) hydration of this ion to a hydrogen ortho ester, and (3) breakdown of the latter to alcohol and carboxylic acid ester products (eq 1–3).[1] This reaction mechanism, though quite reasonable, is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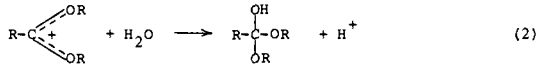
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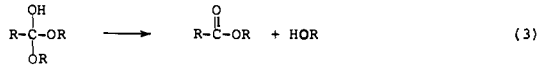
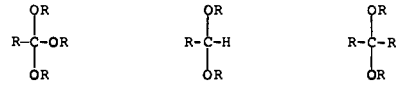

(3)

based upon kinetic information, which, until very recently, was obtained under conditions where the first stage is rate determining; there was therefore no direct kinetic evidence for the rest of the reaction scheme. In a preliminary account of the present study,[2] we reported that we discovered conditions under which, with certain substrates, the third stage of this three-stage sequence is rate determining. This enabled us to detect the dialkoxycarbonium ion intermediates in these reactions, to estimate rate and equilibrium constants for their decay to hydrogen ortho esters, and to measure rate constants for the conversion of the latter to ultimate reaction products. We thus provided direct kinetic evidence for the full reaction scheme. We now describe that work in full.

Ortho esters (**1**) are trigeminal ethers, and their chemistry is quite similar in many respects to that of their geminal ether analogues, acetals (**2**) and ketals (**3**). The latter two, like ortho


1 **2** **3**

esters, undergo facile acid-catalyzed hydrolysis, and this is also a three-stage process involving two reaction intermediates quite similar to those of eq 1–3: monoalkoxycarbonium ions are formed as the counterparts of the dialkoxycarbonium ions generated in eq 1, and these are hydrated to hemiacetals or hemiketals as the analogues of the hydrogen ortho esters formed in eq 2.[1] Much new insight into the nature of these hydrolyses has been gained through the recent detection of these two kinds of intermediates as transient species formed in certain examples of these reactions. Thus, hemiacetals have been detected in the hydrolysis of strained acetals in which one of the alkoxy groups is part of a three-membered[3] or four-membered[4] ring, or in which both alkoxy groups are unusually bulky;[5] very recently, hemiacetals were even discovered in the hydrolysis of simple aromatic acetals such as benzaldehyde diethyl acetal.[6] Hemiacetals have also been found in the hydrolysis of acylals,[7] and hydrogen ortho esters have been found in the hydrolysis of acyloxy ortho esters.[8] Oxocarbonium ions have also been detected in some ortho ester and ketal hydrolyses: dialkoxycarbonium ions in the case of aromatic ortho esters[9] and alkoxytropylium and alkoxydiphenylcyclopro-

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