Ester Aminolysis in the Presence of Alkylammonium Carboxylate Reversed Micelles. A Mechanistic Study

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Synopsis. A study of ester aminolysis in the presence of dodecylammonium carboxylate reversed micelles showed that the catalytic role of the surfactant head-anion (general base) was concentration independent. The presence of co-solubilized water in the micelle did not lead to detectable ester hydrolysis.

Several types of reactions were found to be catalyzed by reversed micelles (RM's).[2,3] Ester aminolysis in the presence of alkylammonium carboxylate RM's has received a fair amount of attention.[4-7] Evidence has been given to show that the carboxylate ion of the surfactant is acting as a general base,[7b] not as a nucleophile.[6] In these reactions the ratio [detergent]/[ester] is usually large (typically ≥50). It has been argued, however, that the nucleophilic catalysis pathway can still occur if a much lower [surfactant]/[ester] ratio were used.[8] This implies that a change in the reaction mechanism (from general base to nucleophilic catalysis) can be induced by changing the concentration ratio of the reactants.[9] We checked, therefore, the concentration dependence of the catalytic role of the carboxylate ion of these surfactants and the conditions under which it can act as a nucleophile.

As recently argued,[8] co-solubilization of water in the core of the RM can lead to the occurence of hydrolysis as a competing reaction. This is not in agreement with our study of ester aminolysis in the presence of dodecylammonium diethylarsinate RM's.[7a] Since the carboxylate ion is a much weaker base than the diethylarsinate ion[11] we sought direct evidence for, or against, the occurence of hydrolysis in the case of the present RM's.

Results and Discussion

Consider the aminolysis of *p*-nitrophenyl *p*-nitrobenzoate by dodecylammonium *p*-anisate (DAPA) RM's or by a mixture of DAPA and dodecylamine (DA). The nucleophilic catalysis mechanism should proceed via attack of the *p*-anisoyloxy group on the ester to give the intermediate anhydride $O_2NC_6H_4CO\cdot O\cdot OCC_6H_4OCH_3$ whose aminolysis should yield a mixture of the amides $O_2NC_6H_4CONHC_{12}H_{25}$ and $CH_3OC_6H_4CONHC_{12}H_{25}$.[8] According to the general base catalysis mechanism only one amide, that derived from the ester, i.e., $O_2NC_6H_4CONHC_{12}H_{25}$, should be produced[7b] so that analysis of the products should settle the question. Entries 1—3 of Table 1 show the results for the aminolysis by DAPA and by DAPA+DA using small [detergent]/[ester] ratios. Only *N*-dodecyl-*p*-nitrobenzamide was obtained which clearly shows that the catalytic role of the *p*-anisoyloxy group of DAPA is concentration independent.

The question now arises: Under which conditions will the *p*-anisoyloxy group act as a nucleophile in the micellar core? Recently it has been shown that the acetate ion of $(CH_3)_4N^+{}^-O_2CCH_3$ reacts with esters in aprotic solvents producing mixed anhydrides.[13] We decided, therefore, to investigate whether the same result will be obtained in the presence of the surfactant. Entries 4—7 of Table 1 show the results of the reaction of the benzoate ester with DAPA and with DAPA+DA in the presence of tetramethylammonium *p*-anisate (TMA) in CH_3CN and in CH_2Cl_2. The *p*-anisoyloxy group acted as a nucleophile (as shown by the production of amides A,B) only under the condition [TMA]≥[DAPA]. While the formation of RM's in CH_3CN may be dubious[3] the reaction in CH_2Cl_2 is certainly taking place within the micellar domain since TMA is only soluble in the presence of the surfactant.

The preceding results can be rationalized as follows: In the micellar core the *p*-anisoyloxy group can act as a nucleophile only if it is "naked" or desolvated.[10,13] ^1H NMR data demonstrated that the carboxylate ion is strongly hydrogen-bonded to the alkylammonium ion[3] so that it is present in a protic microenvironment. Note that this hydrogen-bonding is an intrinsic property, i.e., it is neither dependent on the presence of the ester nor on the [detergent]/[ester] ratio. Solubilization of TMA in the RM introduces "excess" *p*-anisate ions which are not hydrogen-bonded to their cations (the $(CH_3)_4N^+$ ions) and is thus expected to favor the nucleophilic catalysis mechanism. That the latter took place only at higher [TMA] is understandable in terms of the ability of the alkylammonium

Table 1. Aminolysis of *p*-Nitrophenyl *p*-Nitrobenzoate in the Presence of Dodecylammonium *p*-Anisate Reversed Micelles in Organic Solvents[a]

Reaction	DAPA[b] mmol	DA[b] mmol	TMA[b] mmol	Amides obtained[c]
1	3.0	—	—	A
2	5.0	—	—	A
3	5.0	2.5	—	A
4	5.0	—	2.8	A
5	5.0	2.5	3.2	A
6	5.0	2.5	5.0	A+B
7	5.0	2.5	8.0	A+B

a) At room temperature, ester=0.8 mmol, in 20 ml CH_2Cl_2 (Reactions 1—7) or acetonitrile (Reactions 4—7). b) For abbreviations see text. c) Determined by ^1H NMR. Amide: A=$O_2NC_6H_4CONHC_{12}H_{25}$; B=$CH_3OC_6H_4CONHC_{12}H_{25}$.

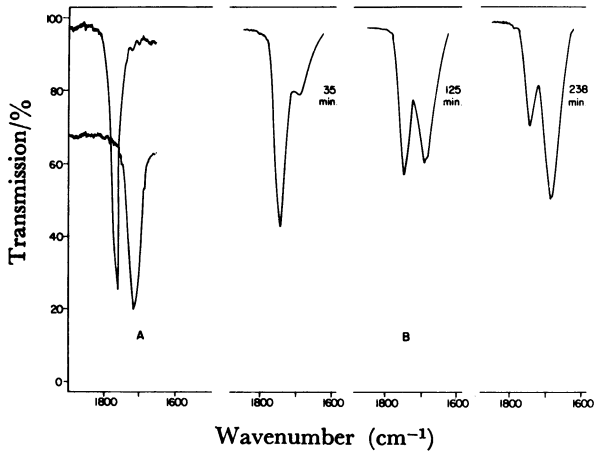

Fig. 1. Part A shows the peaks of the CO groups of methyl *p*-nitrophenyl carbonate and methyl dodecylcarbamate (both 0.05 M) in chloroform. The progress of the reaction of 0.05 M carbonate ester, 0.1 M DAP in the presence of 0.6 M water is shown in part B.

ions to complex more than one carboxylate ion.[14] The relevant point here is that due to the protic nature of the core of alkylammonium carboxylate RM's the possibility that the RCO_2^- group of the surfactant can act as a nucleophile is now essentially excluded.

The aminolysis of methyl *p*-nitrophenyl carbonate in the presence of dodecylammonium propionate (DAP)-solubilized water was studied in chloroform and in toluene. Our choice of this ester was dictated by the favorably large separation between the peaks of the CO groups of the ester (1760 cm^{-1}) and methyl dodecylcarbamate (the product of aminolysis, at 1710 cm^{-1}) as shown in part A of Fig. 1. The reaction progress is shown in part B in which the ester peak gradually disappeared and that due to the aminolysis appeared. Quantitative analysis in both solvents indicated that all the carbonate ester that reacted appeared as amide, i.e., practically no hydrolysis occurred. This is similar to the reaction of alkyl *p*-nitrophenyl carbonates with amines in aqueous solutions where only aminolysis occurs, probably because of the higher reactivity of amines relative to water.[15] Since the head-ions of DAP are strongly hydrogen-bonded it is easy to understand why the carboxylate ion (acting as a general base) accepted a proton from the dodecylammonium ion (leading to aminolysis) rather than from a water molecule (causing hydrolysis).

Experimental

All solvents (Aldrich) were purified and kept on activated 4A molecular sieves. DAP, DAPA, the benzoate, and the carbonate esters, methyl dodecylcarbamate, *N*-dodecyl-*p*-anisamide were obtained as given elsewhere.[5,7] *N*-Dodecyl-*p*-nitrobenzamide was prepared by refluxing DA and benzoyl chloride (molar ratio 2:1) in chloroform and was recrystallized from hexane–chloroform. Mp 96—97 °C. ^1H NMR (Varian T-60 spectrometer, in $CDCl_3$) δ=8.01 (d, 2H), 7.81 (d, 2H), 5.95 (m, 1H), 3.88 (m, 2H), 1.27 (apparent s, 20H), and 0.84 (t, 3H). Found: C, 68.14; H, 8.96; N, 8.29%. Calcd for $C_{19}H_{30}N_2O_3$: C, 68.26; H, 8.98; N, 8.38%. TMA was prepared by carefully neutralizing tetramethylammonium hydroxide with *p*-anisic acid in aqueous methanol. Prolonged drying in vacuo, over P_2O_5 at 70 °C gave the anhydrous salt. ^1H NMR (CD_3CN) δ=7.71 (d, 2H), 6.85 (d, 2H), 3.81 (s, 3H), and 3.21 (s, 12H). This hygroscopic salt was handled in Atomsbag (Aldrich) and was dried to a constant weight before being used. A typical aminolysis reaction in CH_2Cl_2 was as follows: The reactants were stirred overnight under N_2, the organic solution was washed with NaOH (pH=11) until the latter was colorless, with water, dried, and the solvent removed. The solid residue was washed with hexane, dried, then submitted to analysis by ^1H NMR.

IR spectra were obtained with a Perkin-Elmer 238 spectrometer using 0.2 mm CaF_2 cells. Quantitative analysis were carried out using the absorption mode. The concentrations of the reacting ester and of the produced carbamate were determined from the corresponding Beer's law plots (using peak areas and/or weights), and were accurate to ±2%.

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References

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2) Detergent aggregates in organic solvents are termed reversed micelles. Chemical reactions usually take place at the central part, or core, of the RM. This part is surrounded by the surfactant head groups.[3]

3) J. H. Fendler, "Membrane Mimetic Chemistry," Wiley, N. Y. (1982).

4) K. Kon-no, T. Matsuyama, H. Mizuno, and K. Kitahara, *Nippon Kagaku Kaishi*, **1975**, 1857.

5) O. A. El Seoud, A. Martins, L. P. Barbur, M. J. da Silva, and V. Aldrigue, *J. Chem. Soc., Perkin Trans. 2*, **1977**, 1674.

6) C. J. O' Connor and R. E. Ramage, *Aust. J. Chem.*, **33**, 757 (1980).

7) a) M. I. El Seoud and O. A. El Seoud *J. Org. Chem.*, **46**, 2686 (1981); b) M. I. El Seoud, R. C. Vieira, and O. A. El Seoud, *ibid*, **47**, 5137 (1982).

8) C. J. O'Connor, T. D. Lomax, and R. E. Ramage, *Adv. Colloid Interface Sci.*, **20**, 21 (1984).

9) It is possible, however, to change the nature of the rate limiting step by changing the relative concentrations of the reactants.[10]

10) a) F. M. Menger and A. C. Vitale, *J. Am. Chem. Soc.*, **95**, 4931 (1973); b) U. Tonellato, *J. Chem. Soc., Perkin Trans. 2*, **1978**, 307.

11) Compare, e.g., the pK_a of *p*-anisic acid (4.47) with that of diethylarsinic acid (6.42).[12]

12) E. A. Lewis, L. D. Hansen, E. J. Baca, and D. J. Temer, *J. Chem. Soc., Perkin Trans. 2*, **1976**, 125.

13) J. Hajdu and G. M. Smith, *J. Am. Chem. Soc.*, **103**, 6192 (1981).

14) F. Kohler, R. Gopel, G. Götze, H. Atrops, M. A. Demiriz, E. Liebermann, E. Wilhelm, F. Ratkovics, and B. Palagyi, *J. Phys. Chem.*, **85**, 2524 (1981).

15) M. J. Gressner and W. P. Jencks, *J. Am. Chem. Soc.*, **99**, 6963, 6970 (1977).