nediol. To a stirred suspention of DDQ (1.18 g, 5.2 mmol) and 1,5-pentanediol (0.54 g, 5.2mmol) in benzene (20 mL) was added dropwise over 10 min at 20-25 °C a benzene solution (10 mL) of DDM (1.0 g, 5.2 mmol). After the mixture was stirred for 2 h, $DDQH_2$ was filtered off and was washed with benzene (20 mL × 3). The filtrate parts and the washing were combined, washed with 5% aqueous sodium carbonate (10 mL × 5) and then with NaCl saturated water (10 mL × 5), dried over anhydrous sodium sulfate, and concentrated in vacuo to give a pasty residue. The residue was chromatographed on alumina (300 mesh). Elution gave monomeric acetal **2d** (296 mg, 21%), dimeric acetal **3d** (240 mg, 18%), trimeric acetal **4d** (12 mg, 0.9%), and benzophenone (140 mg, 15%) with a light petroleum-benzene mixture (1:20-1:1) and noncyclic acetal **5d** (260 mg, 30%) with benzene-methanol (100:1). In the case of 1,6-hexanediol and 1,12-dodecanediol, dimeric acetals were partly filtered off together with $DDQH_2$; however, these dimers were cleanly recovered by dissolving $DDQH_2$ in a minimum amount of acetone. The structures of monomeric, dimeric, and trimeric cyclic acetals were determined by IR, NMR, mass spectra, and elemental analyses.

2,2-Diphenyl-1,3-dioxolane (2a): mp 54-55 °C (from ether); IR (KBr) 2800, 1450, 1085, 1000 cm^{-1}; NMR ($CDCl_3$) δ 4.0 (s, 4 H, OCH_2CH_2O), 7.1-7.6 (m, 10 H, Ph); MS, *m/e* 226 (M^+). Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.68; H, 6.24.

2,2-Diphenyl-1,3-dioxane (2b): mp 113-115 °C (from ether); IR (KBr) 2970, 1450, 1100, 1005 cm^{-1}; NMR ($CDCl_3$) δ 1.7-2.0 (m, 2 H, CH_2), 4.03 (t, 4 H, OCH_2, J = 6.0 Hz), 7.1-7.7 (m, 10 H, Ph); MS, *m/e* 240 (M^+). Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.96; H, 6.72. Found: C, 79.88; H, 6.65.

2,2-Diphenyl-1,3-dioxepane (2c): mp 124-126 °C (from ether); IR (KBr) 2880, 1450, 1090, 700 cm^{-1}; NMR ($CDCl_3$) δ 1.5-1.8 (m, 4 H, CH_2CH_2), 3.6-3.9 (m, 4 H, OCH_2), 7.1-7.7 (m, 10 H, Ph); MS, *m/e* 254 (M^+). Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.19; H, 7.03.

2,2-Diphenyl-1,3-dioxocane (2d): mp 41-42 °C (from ether); IR (KBr) 2920, 1440, 1090, 1025 cm^{-1}; NMR ($CDCl_3$) δ 1.5-1.8 (m, 6 H, $(CH_2)_3$), 3.55 (t, 4 H, OCH_2, J = 6.3 Hz), 7.0-7.6 (m, 10 H, Ph); MS, *m/e* 268 (M^+). Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.79; H, 7.49.

2,2,10,10-Tetraphenyl-1,3,9,11-tetraoxacyclohexadecane (3d): mp 217-218 °C (from benzene); IR (KBr) 2930, 1440, 1080, 1020 cm^{-1}; NMR ($CDCl_3$) δ 1.2-1.9 (m, 12 H, $(CH_2)_3$), 3.23 (t, 8 H, OCH_2, J = 6.0 Hz), 7.0-7.7 (m, 20 H, Ph); MS, *m/e* 536 (M^+). Anal. Calcd for $C_{36}H_{40}O_4$: C, 80.56; H, 7.51. Found: C, 80.60; H, 7.50.

2,2,11,11-Tetraphenyl-1,3,10,12-tetraoxacyclooctadecane (3e): mp 241-243 °C (from $CHCl_3$); IR (KBr) 2930, 1445, 1090, 1020 cm^{-1}; NMR ($CDCl_3$) δ 1.3-1.9 (m, 16 H, $(CH_2)_4$), 3.21 (t, 8 H, OCH_2, J = 7.5 Hz), 7.1-7.6 (m, 20 H, Ph); MS, *m/e* 564 (M^+). Anal. Calcd for $C_{38}H4_4O_4$: C, 80.81; H, 7.85. Found: C, 80.63; H, 7.86.

2,2,12,12-Tetraphenyl-1,3,11,13-tetraoxacycloeicosane (3f): mp 181-183 °C (from benzene); IR (KBr) 2930, 1445, 1090, 1025 cm^{-1}; NMR ($CDCl_3$) δ 1.2-1.8 (m, 20 H, $(CH_2)_5$), 3.21 (t, 8 H, OCH_2, J = 6.6 Hz), 7.2-7.7 (m, 20 H, Ph); MS, *m/e* 592 (M^+). Anal. Calcd for $C_{40}H_{48}O_4$: C, 81.04; H, 8.16. Found: C, 81.05; H, 8.14.

2,2,13,13-Tetraphenyl-1,3,12,14-tetraoxacyclodocosane (3g): mp 220-222 °C (from benzene); IR (KBr) 2940, 1445, 1090, 1030 cm^{-1}; NMR ($CDCl_3$) δ 1.1-1.9 (m, 24 H, $(CH_2)_6$), 3.23 (t, 8 H, OCH_2, J = 6.3 Hz), 7.0-7.6 (m, 20 H, Ph); MS, *m/e* 620 (M^+). Anal. Calcd for $C_{42}H_{52}O_4$: C, 81.25; H, 8.44. Found: C, 81.43; H, 8.45.

2,2,14,14-Tetraphenyl-1,3,13,15-tetraoxacyclotetracosane (3h): mp 103-104 °C (from $CHCl_3$); IR (KBr) 2920, 1445, 1090, 1020 cm^{-1}; NMR ($CDCl_3$) δ 1.2-1.9 (m, 28 H, $(CH_2)_7$), 3.19 (t, 8 H, OCH_2, J = 6.8 Hz), 7.1-7.7 (m, 20 H, Ph); MS, *m/e* 648 (M^+). Anal. Calcd for $C_{44}H_{56}O_4$: C, 81.44; H, 8.70. Found: C, 81.31; H, 8.71.

2,2,15,15-Tetraphenyl-1,3,14,16-tetraoxacyclohexacosane (3i): mp 171-172 °C (from $CHCl_3$); IR (KBr) 2930, 1450, 1085, 1020 cm^{-1}; NMR ($CDCl_3$) δ 1.1-1.8 (m, 32 H, $(CH_2)_8$), 3.20 (t, 8 H, OCH_2, J = 6.2 Hz), 7.1-7.6 (m, 20 H, Ph); MS, *m/e* 676 (M^+). Anal. Calcd for $C_{46}H_{60}O_4$: C, 81.61; H, 8.93. Found: C, 81.79; H, 8.99.

2,2,17,17-Tetraphenyl-1,3,16,18-tetraoxacyclotriacosane (3j): mp 85-86 °C (from $CHCl_3$); IR (KBr) 2920, 1445, 1090, 1020 cm^{-1}; NMR ($CDCl_3$) δ 1.1-1.8 (m, 40 H, $(CH_2)_{10}$), 3.20 (t, 8 H, OCH_2, J = 6.5 Hz), 7.1-7.7 (m, 20 H, Ph); MS, *m/e* 733 (M^+). Anal. Calcd for $C_{50}H_{68}O_4$: C, 81.92; H, 9.35. Found: C, 81.62; H, 9.37.

2,2,10,10,18,18-Hexaphenyl-1,3,9,11,17,19-hexaoxacyclotetracosane (4d): mp 76-79 °C (from benzene-pentane); IR (KBr) 2940, 1450, 1080, 1020 cm^{-1}; NMR ($CDCl_3$) δ 1.1-1.9 (m, 18 H, $(CH_2)_3$), 2.9-3.4 (m, 12 H, OCH_2), 6.9-7.7 (m, 30 H, Ph); MS, *m/e* 804 (M^+). Anal. Calcd for $C_{54}H_{60}O_6$: C, 80.56; H, 7.51. Found: C, 80.60; H, 7.59.

The resinous noncyclic acetals showed the characteristic IR absorption assignable to hydroxyl groups (3350-3370 cm^{-1}) and ethereal bonds (1000-1200 cm^{-1}). The NMR spectra of these compounds revealed the presence of aromatic rings ($CDCl_3$, δ 7.1-7.6 ppm), hydroxyl groups (2-3 ppm), and three kinds of methylenes respectively assignable to central methylene moieties (1.2-1.8 ppm), OCH_2 (3.1-3.3 ppm), and CH_2OH (3.5-3.7 ppm). It is difficult to purify these resinous products so that further structural evidence was offered by the conversion into dimeric acetal when treated with excess DDM and DDQ (vide infra).

Reaction of DDM with DDQ Followed by Addition of 1,12-Dodecanediol. To a stirred suspension of DDQ (1.18 g, 5.2 mmol) in benzene (20 mL) was added dropwise over 10 min at 20 °C a benzene solution (10 mL) of DDM (1.0 g, 5.2 mmol). Introduction of an equivalent amount of powdered diol was made step by step over 1 h, causing gradually the precipitation of $DDQH_2$. After 1 h of stirring, usual workup of the reaction mixture provided **3j** (0.35 g, 18%) and **5j** (0.65 g, 44%).

Conversion of Noncyclic Acetals 5 into Dimeric Cyclic Acetals 3. This conversion was demonstrated in the case of noncyclic acetal **5g** of 1,8-octanediol by the use of 2 equiv of DDM and DDQ. To a stirred suspension of DDQ (0.59 g, 2.6 mmol) and **5g**, (0.6 g, 1.3 mmol) in benzene (10 mL) was added dropwise over 10 min at 20 °C a benzene solution (5 mL) of DDM (0.5 g, 2.6 mmol). After the mixture was stirred for 2 h, usual workup gave **2g** in 80% yield. The successful conversion of other noncyclic acetals also provided the corresponding dimeric acetals in over 60-80% yields.

Acid-Catalyzed Hydrolysis of Dimeric Actals 3d-i. Kinetic measurements were made by monitoring the decrease in the respective absorption of **3d-i** at 254 nm by means of high-performance liquid chromatography with methanol as an eluent.

A pseudo-first-order treatment of these analytical data gave the observed rate constants (k_{obsd}) for each of **3d-i** according to eq 3.

$$-\frac{d[3]}{dt} = k[H^+][3] = k_{obsd}[3] \qquad (3)$$

Registry No. **1a**, 107-21-1; **1b**, 504-63-2; **1c**, 110-63-4; **1d**, 111-29-5; **1e**, 629-11-8; **1f**, 629-30-1; **1g**, 629-41-4; **1h**, 3937-56-2; **1i**, 112-47-0; **1j**, 5675-51-4; **2a**, 4359-34-6; **2b**, 786-03-8; **2c**, 77130-20-2; **2d**, 91491-62-2; **3d**, 91491-63-3; **3e**, 91491-64-4; **3f**, 91491-65-5; **3g**, 91491-66-6; **3h**, 91491-67-7; **3i**, 91491-68-8; **3j**, 91491-69-9; **4d**, 91491-70-2; **5d**, 91491-71-3; **5e**, 91491-72-4; **5f**, 91491-73-5; **5g**, 91491-74-6; **5h**, 91491-75-7; **5i**, 91491-76-8; **5j**, 91491-77-9; DDM, 883-40-9; DDQ, 84-58-2.

Ester Aminolysis in the Presence of Alkylammonium Carboxylate Reversed Micelles. On the Nature of the Rate-Limiting Step

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We have been interested in studying the mechanisms of reactions catalyzed by the reversed micelles[1] of alkyl-

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[1] Reversed micelles are aggregates of surfactants in nonaqueous solvents. The central part or "core" of the aggregate is made of the hydrophilic groups of the surfactant and is the site of solubilization and chemical reactions.[2,3]

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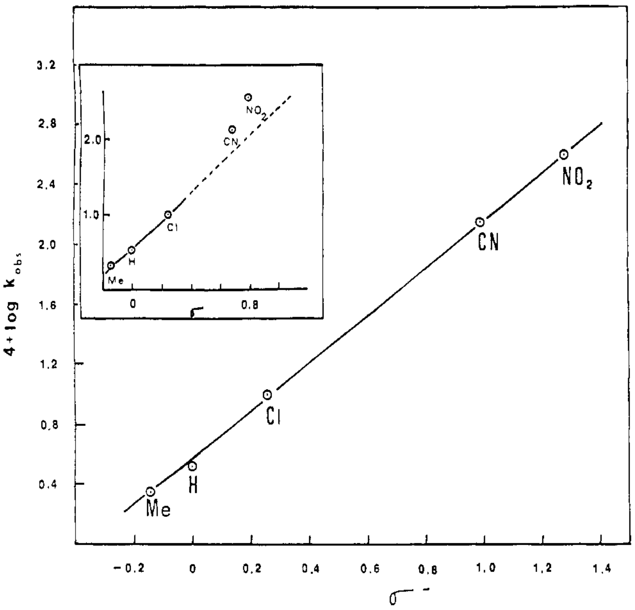


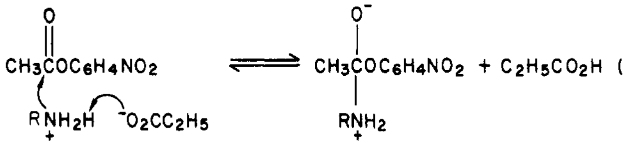
Figure 1. The Hammett equation plot for the $NO_2C_6H_4CO_2$-C_6H_4Y series.

Table I. Observed Rate Constants for the Reaction of the $XC_6H_4CO_2C_6H_4Y$ Esters with DAP and with DA + DAP, in Cyclohexane, at 25 °C

X/Y	k_{obsd},[a] [DAP] 0.1 M	k_{obsd},[a] [DAP] 0.2 M	k_{obsd},[a] DA + DAP[b]
NO_2/NO_2	124.0	393.0	366.0
Cl/NO_2	8.10	21.80	22.30
H/NO_2	2.90	9.30	8.52
CH_3/NO_2	1.75	4.90	4.36
CH_3O/NO_2	1.0	2.81	2.50
NO_2/CN	54.0	145.0	142.0
NO_2/Cl	4.20	10.20	8.80
NO_2/H	1.48	3.29	2.60
NO_2/CH_3	0.95	2.20	1.60
ρ_X	2.012 ± 0.004	2.043 ± 0.007	2.076 ± 0.005
ρ_Y[c]	1.517 ± 0.001	1.593 ± 0.001	1.681 ± 0.002
ρ_Y[d]	2.25 ± 0.01	2.36 ± 0.03	2.50 ± 0.02
ρ_Y/ρ_X[e]	1.12	1.16	1.20

[a] $10^{-4}\ k_{obsd}$, s^{-1}. [b] [DA] = 0.025 M, [DAP] = 0.1 M, at 30 °C for the $XC_6H_4CO_2C_6H_4NO_2$ series and at 25 °C for the $NO_2C_6H_4CO_2$-C_6H_4Y series. [c] Hammett ρ values based on the σ_p^- scale. [d] Hammett ρ value using σ_p. [e] Using ρ_Y based on σ_p.

ammonium salts.[4,5] Concerning ester aminolysis it has been demonstrated that solubilization of water in the core of the aggregate does not lead to hydrolysis as a competing reaction.[4,5a] We have also presented evidence showing that the anion of the surfactant is acting as a general base,[5b] and not as a nucleophile.[6] The detergent dodecylammonium propionate (DAP) has been most extensively used as a catalyst.[2-6] Ester aminolysis by this surfactant is shown in eq 1 and 2, using p-nitrophenyl acetate as an example; where R = $C_{12}H_{25}$. Based on the reaction of a series of para-substituted phenylacetates, it was suggested that the collapse of the intermediate (eq 2) is rate limiting. This suggestion can be tested by examining the susceptibility of the reacting esters to variations in the structure of the acyl group and/or the leaving group (LG, phenol). Since phenyl acetates are not amenable to this type of study, we prepared two series of benzoate esters p-$XC_6H_4CO_2C_6H_4$-p-NO_2 (X = CH_3O, CH_3, H, Cl, NO_2) and p-$NO_2C_6H_4CO_2C_6H_4$-p-Y (Y = CH_3, H, Cl, CN, NO_2) and studied their aminolysis by dodecylamine (DA), DAP, and by DA + DAP in cyclohexane. Application of the Hammett equation to the kinetic results showed that our idea concerning the nature of the slow step, i.e., eq 2, is correct.



$$CH_3\overset{O}{\overset{\|}{C}}OC_6H_4NO_2 \;\; R\overset{+}{N}H_2H \;\; ^-O_2CC_2H_5 \rightleftharpoons CH_3\underset{R\overset{+}{N}H_2}{\overset{O^-}{C}}OC_6H_4NO_2 + C_2H_5CO_2H \quad (1)$$

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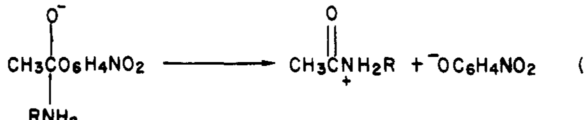
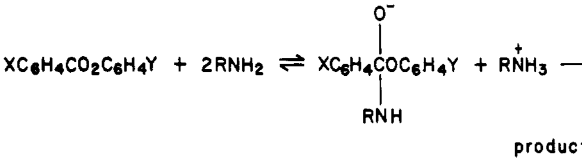


$$CH_3\underset{R\overset{+}{N}H_2}{\overset{O^-}{C}}O_6H_4NO_2 \longrightarrow CH_3\overset{O}{\overset{\|}{C}}\overset{+}{N}H_2R + {}^-OC_6H_4NO_2 \quad (2)$$

Results and Discussion

Aminolysis of $XC_6H_4CO_2C_6H_4Y$ (X/Y = NO_2/NO_2, NO_2/CN, Cl/NO_2) by DA in cyclohexane is second order in the amine. From the known σ_p values[7] we calculated that ρ_X (acyl group variable) and ρ_Y (phenol variable) were 1.47 and 3.52, respectively,[8] giving ρ_Y/ρ_X = 2.39. This large ratio clearly indicates that the reaction is much more sensitive to the nature of the LG than to that of the acyl group, showing that the collapse of the anionic intermediate of eq 3 is rate limiting.[9]



$$XC_6H_4CO_2C_6H_4Y + 2RNH_2 \rightleftharpoons XC_6H_4\underset{RNH}{\overset{O^-}{C}}OC_6H_4Y + R\overset{+}{N}H_3 \longrightarrow \text{products} \quad (3)$$

Table I shows the observed rate constants (k_{obsd}) for the reaction of the benzoate esters with DAP and with DA + DAP, along with the corresponding ρ_X and ρ_Y values. The Hammett equation plot for the $NO_2C_6H_4CO_2C_6H_4Y$ series is shown in Figure 1. The insert in Figure 1 clearly shows that the use of σ_p^- is more appropriate. This indicates that the LG is phenoxide ion rather than the phenol. In order to be able to compare the data of the two ester series we have calculated ρ_Y using σ_p and the results are given in Table I.[12]

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(2) Menger, F. M. *Pure Appl. Chem.* **1979**, *51*, 999. Kitahara, A. *Adv. Colloid Interface Sci.* **1980**, *12*, 109.

(3) Fendler, J. H.; Fendler, E. J. "Catalysis in Micellar and Macromolecular Systems"; Academic Press: New York, 1975. Fendler, J. H. "Membrane Mimetic Chemistry"; Wiley: New York, 1982.

(4) El Seoud O. A.; Martins, A.; Barbur, L. P.; da Silva, M. J.; Aldrigue, V. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1674. El Seoud, O. A.; Pivêtta, F.; El Seoud M. I.; Farah, J. P. S.; Martins A. *J. Org. Chem.* **1979**, *44*, 4832.

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

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

(7) Exner, O. "Correlation Analysis in Chemistry"; Chapman, N. B., Shorter, J., Eds.; Plenum Press: New York, 1978.

(8) Based on the following rate constants at 30 °C: 0.1129, 0.0463, and 0.0165 $M^{-2}\ s^{-1}$ for X/Y = NO_2/NO_2, NO_2/CN, and Cl/NO_2, respectively.

(9) In eq 3 the second amine molecule is shown to act as a general base for the amine attack, as given elsewhere.[4,5,10] Note that according to the principle of microscopic reversibility the anionic intermediate can revert back to reactants by accepting a proton from the formed R^+NH_3 ion. Therefore for the reverse reaction the leaving group will be RNH_2, and not RNH^- as previously argued.[11]

(10) Singh, T. D.; Taft, R. W. *J. Am. Chem. Soc.* **1975**, *97*, 3867. Rivetti, F.; Tonellato, U., *J. Chem. Soc., Perkin Trans. 2* **1977**, 1176. Tonellato, U. *Ibid.* **1978**, 307.

(11) Menger, F. M.; Smith, J. H. *J. Am. Chem. Soc.* **1972**, *94*, 3824.

(12) The standard deviations in ρ_Y (based on σ_p or on σ_p^-) may not clearly show the improvement in the quality of fit of the experimental points to the straight lines. However, the sum of the squares of the residues (corresponding to the differences between the experimental and theoretical values of log k_{obsd}) shows this. For example, for the aminolysis by 0.2 M DAP the sums are 0.053 and 0.004 for σ_p, and σ_p^-, respectively. Note that the data for ester aminolysis in aprotic solvents also correlate better with σ_p^- (LG variable).[11]

Table II. Dependence of the Values of ρ on the Concentration of Solubilized Water[a]

H_2O, M	ρ_X	ρ_Y^b	ρ_Y/ρ_X
0	2.043	2.36	1.16
0.1	1.848	2.58	1.40
0.2	1.877	2.72	1.45
0.3	1.848	2.80	1.51
0.4	1.910	2.86	1.50
0.6	1.910	2.94	1.54
0.8	1.877	2.97	1.58

[a] [DAP] = 0.2 M, at 35 °C in cyclohexane. [b] Based on σ_p.

As expected, both ρ_X and ρ_Y were independent of the concentration of the surfactant since we have less than one ester molecule/DAP aggregate. Consequently, ester solubilization is not likely to change the nature of the reaction site, i.e., the micellar core (however, vide infra when water was solubilized). The fact that $\rho_Y > \rho_X$ shows that the reaction is more susceptible to the nature of the LG and is in agreement with eq 2 representing the rate limiting step. Two important differences exist, however, between the results of aminolysis by DA in cyclohexane and by DAP or by DA + DAP in the same solvent. First the values of ρ_X and ρ_Y are different, and the micellar ρ_Y/ρ_X ratios are, at a first glance, disappointingly small. The nature of the reaction "medium" is, however, very different in both cases. Unlike the nonpolar, aprotic cyclohexane, the micellar core is protic and highly polar.[2,13] As a consequence the ionic tetrahedral intermediates, and the incipient transition states, will most likely be H-bonded to the DAP headions.[14] In fact, only in cyclohexane is the aminolysis by DAP second order in the surfactant,[2,5] showing that the intermediate I of eq 1 is associated with a second molecule of the detergent. This H-bonding will stabilize the transition state and attenuate the dependence of k_{obsd} on the nature of the LG, i.e., decrease ρ_Y.

The preceding idea can be neatly verified by examining the behavior of ρ_X and ρ_Y when the H-bonding ability of DAP is progressively decreased. Solubilization of water is known to hydrate the $^+NH_3$ and CO_2^- groups of DAP and to decrease their tendency to form H-bonds.[1,2,13] We have studied the aminolysis of 3 esters (X/Y = H/NO_2; NO_2/H; NO_2/NO_2) by DAP in the presence of solubilized water and the results are given in Table II. The remarkable feature of this table is the constancy of ρ_X as a function of increasing the concentration of the solubilized water. On the other hand, ρ_Y (and hence ρ_Y/ρ_X) steadily increased. From this table it is clear that as the H-bonding ability of DAP decreases (due to its hydration), the reaction becomes more sensitive to the structure of the LG, as argued before. The fact that only ρ_Y showed a noticeable dependence on [H_2O] is in clear agreement with eq 2 being the slow step.[16] Compared to acyl transfer reactions in bulk organic solvents,[10,11] it seems, therefore, that the observed enhancement of the reaction rates by micellar alkylammonium carboxylates[2-6] is not due to changes either in the reaction mechanism or in the nature of the slow step.

Experimental Section

Cylohexane (Merck) was kept on activated 4-Å molecular sieves; DA (Merck) was distilled from CaH_2. DAP was prepared as given elsewhere[15] and dried to a constant weight in vacuo, over P_2O_5. The esters were prepared by refluxing the appropriate acyl chloride (from the acid and $SOCl_2$)[18] and sodium phenoxide (from the phenol and NaH)[18] in dichloroethane for 5 h. After filtration of the precipitated NaCl, and evaporation of the solvent, the crude esters were crystallized from ethanol–hexane. Their purity was established from their melting points[11,19] and ^1H NMR spectra.

Ester aminolysis was studied with a Zeiss PM6KS spectrophotometer under pseudo-first-order conditions as given before.[4,5] The values of k_{obsd} were obtained from the absorbance–time data with a Burroughs 6900-B computer. The percentage relative standard deviation of k_{obsd} (i.e., the standard deviation × 100/k_{obsd}) was <2%.

Acknowledgment. We thank the CNP_q and FAPESP Research Foundations for financial support and Maria T. Miranda and Paula P. Brotero for their excellent technical assistance.

Registry No. DA, 124-22-1; DAP, 17448-65-6; $O_2NC_6H_4$-*p*-$CO_2C_6H_4$-*p*-NO_2, 1037-31-6; ClC_6H_4-*p*-$CO_2C_6H_4$-*p*-NO_2, 6264-29-5; $PhCO_2C_6H_4$-*p*-NO_2, 959-22-8; $H_3CC_6H_4$-*p*-$CO_2C_6H_4$-*p*-NO_2, 15023-67-3; $H_3COC_6H_4$-*p*-$CO_2C_6H_4$-*p*-NO_2, 7464-46-2; $O_2NC_6H_4$-*p*-$CO_2C_6H_4$-*p*-CN, 32792-81-7; $O_2NC_6H_4$-*p*-$CO_2C_6H_4$-*p*-Cl, 7511-31-1; $O_2NC_6H_4$-*p*-CO_2Ph, 1429-05-6; $O_2NC_6H_4$-*p*-$CO_2C_6H_4$-*p*-CH_3, 15024-11-0.

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(13) Fendler, J. H.; Liu, L. J. *J. Am. Chem. Soc.* **1975**, *97*, 999.

(14) ^1H NMR studies[15] have clearly shown the strong H-bonding ability of alkylammonium carboxylate reversed micelles in organic solvents.

(15) El Seoud, O. A.; Fendler, E. J.; Fendler, J. H. *J. Chem. Soc.*, Faraday Trans. 1 **1974**, *70*, 549. El Seoud, O. A.; Ribeiro, F. P. *J. Org. Chem.* **1976**, *41*, 1365.

(16) It has been argued that the aggregation number of DAP reversed micelles increases as a function of increasing R.[17a] Evidence to the contrary is also available.[17b] It is not expected, however, that any changes in the micellar parameters due to water solubilization will affect the validity of the preceding discussion. The similarity of the structures of the series of esters used here guarantees that any additional perturbance (for example, that induced by water solubilization) will affect ρ_x, ρ_y, and hence their ratio, in a similar way.

(17) (a) Correll, G. D.; Cheser, R. N., III; Nome, F.; Fendler, J. H. *J. Am. Chem. Soc.* **1978**, *100*, 1254. (b) Senō, M.; Araki, K., Shiraishi, S. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 899.

(18) The melting points of most of these substituted acids and phenols did not correspond to those specified by the supplier (Aldrich). They were purified by crystallization.

(19) Satchell, D. P. N.; Secemski, I. I. *J. Chem. Soc. B* **1970**, 1013. Kirsch, J. F.; Clewell, W.; Simon, A. *J. Org. Chem.* **1968**, *33*, 127.

Nucleophilic Aromatic Substitution in the Pyrrole Ring: Leaving Group Effect

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In nucleophilic aromatic substitutions the leaving group order $NO_2 \gg Cl > Br$ is commonly observed when anionic nonpolarizable nucleophilic reagents such as methoxide ion react with activated aromatic derivatives such as 1-X-2,4-dinitrobenzenes[1] or 1-X-4-nitrobenzenes.[2] The greater reactivity of the nitro group reflects a two-step addition–elimination mechanism, in which the attachment of the nucleophile to the aromatic ring is the rate-determining step. The high rate of attachment to the NO_2-bearing position can thus be explained on the basis of the ipso effect: the highly electronegative nitro group favors the formation of a bond between the anionic nucleophile and the ipso carbon atom, which has a relatively low electron density.[1]

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(1) Bartoli, G.; Todesco, P. E. *Acc. Chem. Res.* **1977**, *10*, 125.

(2) Bolto, B. A.; Miller, J. *Aust. J. Chem.* **1956**, *9*, 74.

0022-3263/84/1949-4065$01.50/0