water. If one defines $k_1 = k_{-1} = k_{int}$ at $\Delta pK = 0$ as the intrinsic rate constant of the reaction, we note that k_{int} increases about fivefold in 50% Me_2SO. If the lower temperature in 50% Me_2SO is taken into account, the true increase in the intrinsic rate constant is probably closer to a factor of 10.

This increase is consistent with similar findings by others.[3-5] It supports the notion that solvational reorganization is at least part of the reason[3-7] why proton transfers in water involving carbon acids are frequently much slower than those involving "normal"[14] acids. Note, however, that the effect of adding 50% Me_2SO is quite small compared to the effect of changing from water to pure Me_2SO. For example, the rate of deprotonation of arylnitromethanes by phenoxide ion in pure Me_2SO is, for a given ΔpK, about 10^5 times faster than that in water.[5]

On the other hand, our results compare well with the 14-fold increase in the deprotonation rate of nitroethane by acetate ion in ~50% aqueous Me_2SO (mole fraction = 0.20), a solvent in which ΔpK is virtually the same as in water.[4] The smallness of the effect in 50% Me_2SO indicates that, as long as the solvent contains a significant mole fraction of water, its properties with respect to solvational reorganization are mainly governed by the protic component. This is consistent with the well-known dominance of the protic component of mixed protic–dipolar aprotic solvents on other solvational properties, particularly anion solvation as manifested by H_- functions for hydroxide and alkoxide ions.[9]

Another interesting point is that the difference between the rates in 50% Me_2SO and in pure water increases with increasing ΔpK. A possible reason for this trend is that with increasing acidity of the buffer (decreasing ΔpK), hydrogen bonding between the buffer acid and Me_2SO, which is known to be a better hydrogen bond acceptor than water,[15] becomes stronger. If it is necessary to break this hydrogen bond prior to proton transfer to the carbanion, this could lead to an increased activation energy for proton transfer which would become larger for more acidic buffers, thereby partially compensating for the rate enhancing effect of Me_2SO.

Experimental Section

Materials. 1,1-Dinitroethane was prepared by the method of Kaplan and Schechter.[16] The spectrum of the 1,1-dinitroethane anion has a λ_{max} of 381 nm in 50% Me_2SO–50% water (v/v); ϵ was determined to be 1.57×10^4 on a Gilford spectrophotometer.

The buffers were all reagent grade materials and were used without further purification. Reagent grade Me_2SO was stored over molecular sieves.

Solutions: pH and pK_a Measurements. The solutions were prepared by adding the appropriate amounts of aqueous buffer and/or KCl stock solutions to a measured amount of Me_2SO that would correspond to 50% of the final solution volume. To solutions containing the substrate was added 1 equiv of KOH or HCl, respectively, depending on whether the anionic or the neutral form was desired. The pH of the reaction solutions was measured and, where necessary, adjusted to a desired value by doing mock experiments which simulated the conditions in the stopped-flow apparatus. The pH measurements were performed on a Corning Digital 110 pH meter, using a salt bridge containing 50% aqueous Me_2SO saturated with KCl. The pH meter was calibrated with buffers described by Hallé et al.[17]

The pK_a values of the buffers were determined by standard potentiometric procedures, while the pK_a of 1,1-dinitroethane was obtained by standard spectrophotometric procedures.

Rate Measurements. The rates were determined in a Durrum-Gibson stopped-flow spectrophotometer. $1/\tau$ was determined by standard graphical evaluation of the oscilloscope traces.

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Registry No. 1,1-Dinitroethane, 600-40-8; Me_2SO, 67-68-5.

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Kinetics of the Aminolysis and Hydrolysis of *p*-Nitrophenyl Carboxylates in the Presence of Dodecylammonium Propionate and Aerosol-OT Aggregates in Benzene

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Kinetics of the reaction of *p*-nitrophenyl carboxylates with alkylamines (RNH_2; R = butyl, octyl, dodecyl and hexadecyl) and with *N*-alkylimidazoles (RImz; R = methyl, butyl, octyl, dodecyl and hexadecyl) were studied spectrophotometrically in the presence of dodecylammonium propionate (DAP) and bis(2-ethylhexyl) sodium sulfosuccinate (Aerosol-OT or AOT) reversed micelles in benzene. In the pure solvent, aminolysis of *p*-nitrophenyl acetate (NPA) is a function of the amine chain length. In the presence of 0.2 M DAP the reaction is ca. 39 to 50 times faster than that in the absence of the surfactant, due to bifunctional catalysis by the latter. Rates of diazole-catalyzed ester aminolysis (DAP concentration = 0.2 M) decrease with increasing alkyl chain length of both the diazole and/or the ester. Addition of water decreases the observed rates due to hydration of the DAP head groups. In the presence of AOT, the rates of MeImz-catalyzed ester hydrolysis decrease with increasing chain length of the ester alkyl group and increase as a function of added water. This reflects the importance of the substrates distribution between the bulk solvent and the micellar water "pool".

In nonaqueous solvents, several detergents aggregate to form reversed micelles.[1-3] These species have their polar head groups packed around a micellar "core" with the hydrophobic tails in contact with the solvent. Reversed

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micelles can solubilize large amounts of water and organic or inorganic substrates and also catalyze several types of reactions, sometimes dramatically.[4] Catalysis by reversed micelles has been rationalized in terms of enhanced water and substrate reactivities in the micellar core, as well as the occurrence of concerted proton transfer, usually through participation of the surfactant head groups.[4,5] Recently, it was shown that the type of detergent, zwitterionic DAP or anionic AOT, has a marked effect on the rates of the reaction of NPA with dodecylamine, Imz, and MeImz. For example, addition of 0.2 M DAP increases the rate of NPA aminolysis by dodecylamine by a factor of 53, whereas a comparable concentration of AOT decreases the rate by a factor of 2.[6] Little is known, however, with regard to the effect of substrate structure on reversed micellar catalysis. The present paper reports the results of a study of the reaction between a homologous series of *p*-nitrophenyl carboxylates with *n*-alkylamines and/or *N*-alkylimidazoles in the presence of DAP and AOT aggregates in benzene.

The effects of reactant structure on the observed rate behavior serve as a basis for an understanding of the various factors which contribute to catalysis by reversed micelles.

Experimental Section

UV–Vis spectra were recorded at 25 °C, using a Zeiss DMR-10 spectrometer. ^{1}H NMR spectra were obtained with a Varian-T-60 spectrometer; pH measurements were carried out at 25 °C, using a Corning Model 12 pH meter. Benzene, AOT, DAP, and MeImz were purified as before.[3] *N*-Alkylimidazoles were prepared by refluxing the sodium salt of imidazole and the alkyl bromide in THF as given before.[7] *p*-Nitrophenyl carboxylates were prepared by refluxing equimolar amounts of the carboxylic acid and *p*-nitrophenol in the presence of polyphosphate ester (formula Et_3O_3P),[8] as recently published.[9] The purity of these diazoles and esters was established by TLC and from their boiling and/or melting points, ^{1}H NMR, and microanalysis.[7,9]

Distribution coefficients of the esters and/or diazoles between benzene and water were determined as follows. An accurately weighed amount of the substrate was shaken with equal volumes of benzene and water for several hours. After the solution had stood at 25 °C for complete phase separation, samples were withdrawn and analyzed for the substrate. *N*-Alkylimidazoles were titrated against standardized HCl, using methyl orange as indicator.

Carboxylic esters were determined by dissolving the aliquot in nitrogen-saturated borate buffer (pH 9.4) and measuring the liberated phenoxide ion at 400 nm and 25 °C. The concentration of the parent ester was calculated using ϵ = 18 200 M^{-1} cm^{-1}.[10] Apparent pK_a values of *N*-alkylimidazoles were determined at 25 °C in 50% v/v aqueous ethanol at an ionic strength (KCl) of 0.1.

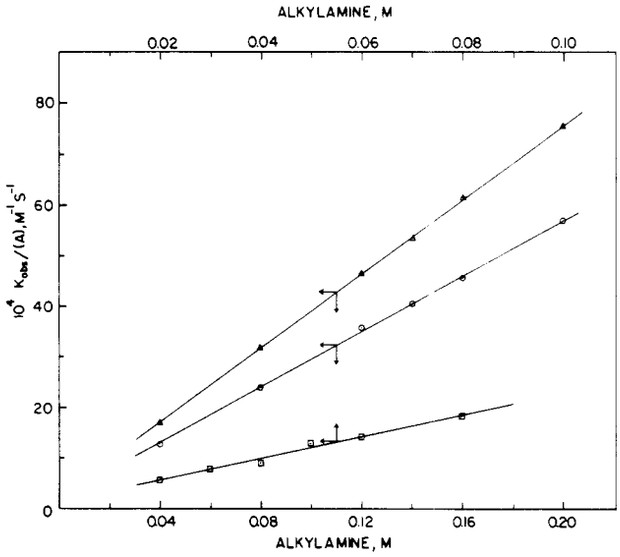

Figure 1. Plots for the aminolysis of NPA (eq 1) by butylamine (⊙), octylamine (△), and hexadecylamine (□) in benzene.

Table I. Rate Constants for NPA Aminolysis by Alkylamines in Pure Benzene and in the Presence of 0.2 M DAP at 25 °C

amine	k_2, M^{-2} s^{-1} [a,b]	k'_2, M^{-2} s^{-1} [a-c]
n-butylamine	0.0276	1.345
n-octylamine	0.0367	1.447
n-dodecylamine	0.0273	1.354
n-hexadecylamine	0.0217	0.968

[a] In most cases, the correlation coefficient of the $k_{obsd}/(a)$ or k_{obsd} vs. (A) graphs was >0.995, and the percentage relative standard deviation of k_2 or k'_2 was <3%. [b] Values of k_1 are 2.0, 2.3, 2.0, and 1.2 × 10^{-4} M^{-1} s^{-1} for butyl-, octyl-, dodecyl-, and hexadecylamine, respectively. [c] The rate constant for ester aminolysis by 0.2 M DAP is 16 × 10^{-4} s^{-1}. This value was substracted from k'_{obsd}.

Kinetic measurements were carried out at 25 °C as before.[6] The ester concentration was 4–8 × 10^{-5} M, that of DAP or AOT was 0.20 M, and the alkylamine concentration range was 0.04–0.20 M in the absence of DAP and 0.02–0.12 M in its presence. Good first-order kinetics were observed, and the pseudo-first-order rate constants (k_{obsd}) were evaluated from the absorbance–time data, using a Hewlett-Packard Model 9820 A calculator or a Burroughs 6700 computer. The percentage relative standard deviation of k_{obsd} (i.e., the standard deviation × $100/k_{obsd}$) was <2.5%.

Results

1. Aminolysis by Alkylamines. The general equation for ester aminolysis is given by[11]

$$k_{obsd} = k_1(A) + k_2(A)^2 \quad (1)$$

where (A) refers to amine; thus a graph of $k_{obsd}/(A)$ vs. (A) should yield a straight line whose slope is k_2 and whose intercept is k_1.[11] Our data fit eq 1, and the results are shown in Figure 1 and the first column of Table I. Due to the small values of k_1, no quantitative significance will be placed on its variation as a function of the amine chain length. The table shows, however, that k_2 increases in going from butyl- to octylamine and then decreases for dodecyl- and hexadecylamine. In the presence of DAP, the reaction is first order in amine. Equation 1 can be modified to account for the catalytic effect of DAP as shown in eq 2. Here k_1 refers to the uncatalyzed reaction

$$k'_{obsd} = k_1(A) + k'_2(A)(M) \quad (2)$$

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Table II. Observed Rate Constants for N-Alkylimidazole-Catalyzed Ester Aminolysis in the Presence of DAP and Solubilized Water in Benzene[a,b]

	$k_{obsd} \times 10^4$, s^{-1} (reaction NPA + RImz)					$k_{obsd} \times 10^4$, s^{-1} (reaction MeImz + RCOO-(p-NO_2-C_6H_4)				
$[H_2O]$, M	MeImz	N-C_4H_9-Imz	N-C_8H_{17}-Imz	N-$C_{12}H_{25}$-Imz	N-$C_{16}H_{33}$-Imz	acetate	butyrate	octanoate	dodecanoate	hexadecanoate
	35.8	31.8	30.0	29.6	28.2	35.8	8.1	8.0	8.0	7.6
0.333	25.8	24.7	23.1	22.2	21.0	25.8	4.6	4.1	3.6	3.0
0.667	17.5	17.7	16.0	15.0	14.0	17.5	2.8	2.3	1.5	1.0
1.0	14.6	14.5	14.0	12.1	11.2	14.6	2.1	1.5	1.1	0.1

[a] Concentrations [DAP] = 0.2 M, [diazoles] = 0.08 M, esters = 6 × 10^{-5} M; temperature = 25 °C. [b] See the Experimental Section for details of the accuracy of k_{obsd}.

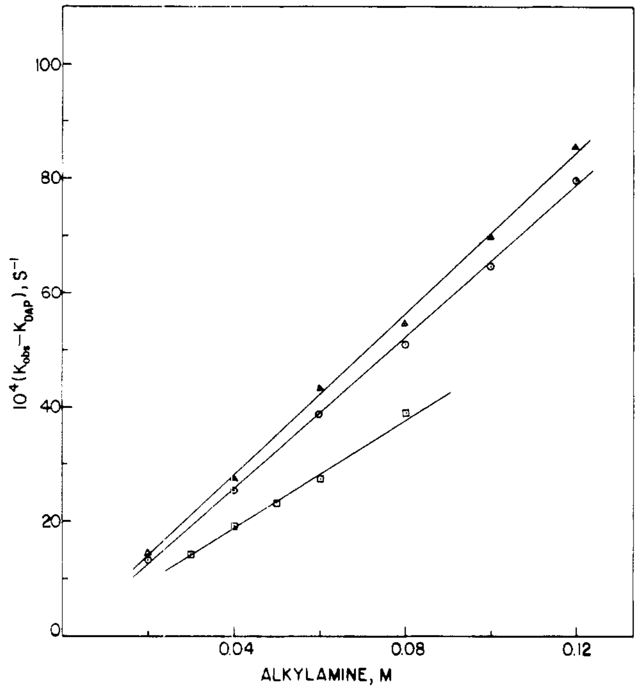

Figure 2. Representative plots of eq 2 showing the aminolysis by butylamine (⊙), octylamine (△), and hexadecylamine (□) in the presence of 0.20 M DAP.

and (M) is the concentration of DAP in the micellar form.[12] A plot of k'_{obsd} vs. (A) in the presence of 0.2 M DAP is linear (Figure 2); k'_2 can be readily obtained from the slope, and the results are given in Table I.[17] Values of k'_2 are always greater than k_2, and their ratios are 48.7, 39.3, 49.6,

(12) Aggregation of alkylammonium carboxylates in organic solvents has been discussed in terms of a single equilibrium model, i.e., monomer ⇌ n-mer association, and a multiple equilibrium model, i.e., monomer ⇌ dimer ⇌ ... ⇌ n-mer.[2,4,13] ^{1}H NMR chemical shifts fit either model equally well, although it appears that the second model has gained more acceptance. The value of (M) in eq 2 is calculated from the equation[2] (M) = $[C_D - \text{cmc}]/N$, where C_D is the detergent concentration, cmc is its critical micelle concentration, and N is its aggregation number. The cmc used here was taken from ref 14 and is an operational value determined from breaks in the graphs of the chemical shifts of the discrete protons of DAP vs. its concentration. It is interesting to note that these operational cmc values correlate well with solvent polarities[3,15] and with the observed rate enhancements.[5,6,16]

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(17) Equation 2 has also been applied at a fixed dodecylamine concentration and a variable DAP concentration.[6] The values of k'_2 obtained in both bases agree well, showing that the alkylamine does not disturb the micelle structure.

Table III. Observed Rate Constants for the Reaction of MeImz with p-Nitrophenyl Carboxylates in the Presence of AOT and Solubilized Water in Benzene[a,b]

	$k_{obsd} \times 10^5$, s^{-1}				
$[H_2O]$, M	acetate	butyrate	octanoate	dodecanoate	hexadecanoate
	2.0	0.87	0.75	0.46	0.30
1.0	8.0	1.25	1.01	0.85	0.60
2.0	10.50	1.68	1.44	1.22	1.08

[a] At 25 °C, [AOT] = 0.2 M and [MeImz] = 0.08 M. [b] See the Experimental Section for details of the accuracy of k_{obsd}.

and 44.6 for butyl-, octyl-, dodecyl-, and hexadecylamine, respectively. As in the previous case, k'_2 reaches a maximum for aminolysis by octylamine.

2. Reaction of p-Nitrophenyl Carboxylates with N-Alkylimidazoles. Observed rate constants for the reaction of NPA with RImz are shown in Table II. They decrease systematically as a function of the increasing chain length of the diazole alkyl group and upon addition of water. In the latter case, rate constants decrease linearly up to a water concentration of 0.667 M, decreasing much more slowly above this concentration. As the table shows, the reaction is more sensitive to addition of water than to the increase of the alkyl group chain length. The effect of increasing the chain length of the ester on the MeImz-catalyzed aminolysis is also demonstrated in Table II.

There is a noticeable rate difference between NPA and the other esters, and this difference increases with increasing water concentration. Thus, in the presence of dry DAP, the ratios k_{NPA}/k_{ester} are 4.4, 4.5, 4.5, and 4.7, whereas in the presence of 1.0 M water, the observed rate constants decreased, and the corresponding ratios are 6.9, 9.7, 13.3, and 146 for p-nitrophenyl butyrate, octanoate, dodecanoate, and hexadecanoate, respectively.

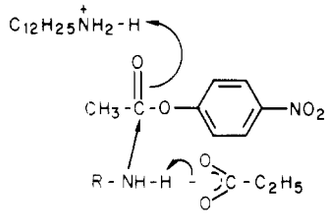
Table III shows the corresponding situation in the presence of 0.20 M AOT. Again, NPA reacts faster than the other esters, and the ratio k_{NPA}/k_{ester} increases as a function of added water. For example, going from dry AOT to detergent containing 1.0 M water, these ratios increase from 2.3, 2.7, 4.3, and 6.7 to 6.4, 7.9, 9.4, and 13.3 for p-nitrophenyl butyrate, octanoate, dodecanoate, and hexadecanoate, respectively. In this case, however, the rate constants *increase* upon addition of water.

Discussion

The predominance of the second term of eq 1 suggests that the principal reaction pathway involves either a general base-catalyzed amine attack or an (kinetically indistinguishable) attack by amine dimers. Published work on the association of aliphatic amines in organic solvents showed, however, no detectable association in the amine concentration range used in our study (0.04–0.2 M).[18]

Moreover, in the presence of DAP the reaction is first order in amine since the surfactant can act as the general base catalyst (vide infra). Table I shows that k_2 is a function of the amine chain length. Taking the value for *n*-butylamine as a reference, the relative rate ratios, $k_{amine}/k_{butylamine}$, are 1.33, 0.99, and 0.78 for octyl-, dodecyl-, and hexadecylamine, respectively. This dependence may be the resultant of small differences in pK_a values and increasing steric hindrance along the amine series.[19]

The appearance of a DAP-containing term in eq 2 lends credence to a mechanism in which the surfactant catalyzes the amine attack by a bifunctional mechanism of the type depicted below:



Based on the above mechanism, k'_2 should be greater than k_2 due to micellar catalysis.[21] Note that although k'_2 and k_2 are maximal for octylamine, the ratio of these rates is, in fact, the smallest of the series. The dependence of k'_2 on the amine chain length can be explained in a manner similar to that used in the pure solvent.

In the presence of DAP, the reaction of NPA with *N*-alkylimidazoles is a diazole-catalyzed ester aminolysis.[6,23] Table II shows that k_{obsd} decreases systematically as a function of increasing chain length of the diazole alkyl group. Because the structure of the latter compounds is very similar, it is possible to use their pK_a values to indicate nucleophilic reactivities inside the micelle. The latter values at 25 °C in 50% aqueous ethanol are 6.45, 6.18, 6.12, and 6.05 for *N*-methyl-, *N*-butyl-, *N*-octyl-, and *N*-dodecylimidazole, respectively. Thus the decrease of k_{obsd} with increasing chain length is in line with the decrease in the pK_a value of the RImz.

Addition of water decreases the observed rates in all cases. This is possibly the result of decreased acid–base catalysis due to the DAP head group hydration or simply to dilution of the reagents in the aggregate core.[25] In addition to ^1H NMR and IR evidence for strong head group hydration,[6,26] the following shows that the former factor is more important. MeImz is much more soluble in water than in benzene, i.e., its concentration in the micellar water pool should increase as water is added. Nevertheless, its rate decreases in a way similar to that of the other alkylimidazoles, which are more soluble in benzene.[27] Second, plots of k_{obsd} vs. water concentration for the diazole-catalyzed reaction are similar to that of the reaction of NPA with DAP. In both cases, k_{obsd} decreases linearly up to a water concentration of 0.667 M, decreasing much more slowly at higher concentrations. For example, the values of k_{obsd} in the dry system and in the presence of 0.333, 0.667, and 1.0 M solubilized water are 35.8, 25.8, 17.5, 14.6×10^{-4} s^{-1} for the MeImz–DAP system (Table II) and 16, 10.7, 7.2, 5.9×10^{-4} s^{-1} for the reaction of NPA with DAP.[6]

The MeImz-catalyzed ester aminolysis is more sensitive, however, to increasing chain length of the carboxylic ester. Thus, in dry DAP solution, NPA reacts ca. 4.5 times faster than the other esters, and this difference increases as water is added. Compared with *N*-alkylimidazoles, carboxylic esters associate weakly with DAP. For example, the constant for association of NPA with DAP is 3.3 times smaller than that for MeImz.[6,28] Moreover, NPA would be expected to bind even less to the hydrated surfactant. These weak interactions with the micelle, coupled with the low solubility in water, may explain the greater sensitivity of k_{obsd} to increasing ester chain length and to added water.[29]

AOT itself does not react with NPA. The reaction with MeImz involves acyl transfer to the diazole, which in the presence of water results in diazole-catalyzed ester hydrolysis. Thus, the UV spectrum of a sample containing NPA, AOT, and imidazole shows a decrease of the ester band at 280 nm and the appearance of a band at 242 nm due to accumulation of the intermediate *N*-acetylimidazole.[30,31] The last peak disappeared rapidly upon addition of water due to hydrolysis of this reaction intermediate. It is thus reasonable to assume that the slow step in the MeImz-catalyzed reaction in the presence of DAP and/or AOT is the same, viz., acyl transfer to the diazole. In view of this consideration, it is interesting to note that the reaction is much slower in the presence of AOT and that addition of water leads to a rate increase. Perhaps the most important factor that contributes to the lower AOT rates is the absence of bifunctional catalysis.

(18) A. E. Lutskii, *Zh. Obshch. Khim.*, **26**, 2299 (1956); *Chem. Abstr.*, **51**, 4977b; J. Fenney and L. H. Sutcliffe, *J. Chem. Soc.*, 1123 (1962); V. F. Bystrov and V. P. Lezina, *Opt. Spektrosk.*, **16**, 430 (1964); H. Wolfe, A. Höpfner, and H. M. Höpfner, *Ber. Bunsenges. Phys. Chem.*, **68**, 410 (1964); C. S. Springer, Jr., and D. W. Meek, *J. Phys. Chem.*, **70**, 481 (1966); H. Shuhr, *Ber. Bunsenges. Phys. Chem.*, **71**, 1104 (1967).

(19) At 25 °C the pK_a values for butyl-, octyl-, dodecyl-, and hexadecylamine are 10.61, 10.65, 10.63, and 10.61.[20] The small differences in the pK_a values may acquire some importance, however, in the absence of the solvent leveling effect.

(20) C. W. Hoerr, M. R. McCorkle, and A. W. Ralston, *J. Am. Chem. Soc.*, **65**, 328 (1943).

(21) The efficiency of this micellar bifunctional catalysis can be clearly demonstrated as follows. At a fixed Imz/surfactant molar ratio of 0.5, DAP increases the observed rate constant by a factor of 344,[6] whereas micellar didodecyldimethylammonium bromide (which cannot transfer protons) increases the rate constant by a factor of 5.[22]

(22) K. Kon-no, A. Kitahara, and M. Fujiwara, *Bull. Chem. Soc. Jpn.*, **51**, 3165 (1978).

(23) That is, it involves nucleophilic catalysis by the diazole and, like the case in aqueous solutions,[24] the slow step is the formation of acetyldiazolium ion. The formation of the latter in the catalysis by Imz–DAP has been verified experimentally.[6]

(24) M. L. Bender, "Mechanisms of Homogeneous Catalysis from Protons to Proteins", Wiley-Interscience, New York, 1971.

(25) It has been shown that solubilization of 0.9 M water in 0.2 M DAP in benzene does not change significantly the aggregation state of DAP.[26] Thus one can assume that the rate decrease is not due to a drastic change in the micellar structure upon solubilization of water.

(26) M. Seno, K. Araki, and S. Shiraishi, *Bull. Chem. Soc. Jpn.*, **49**, 899 (1976).

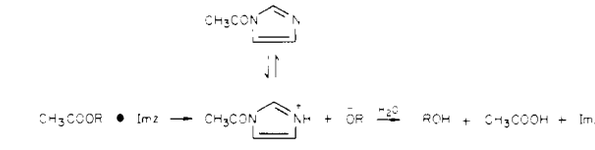
(27) For example, the distribution coefficient, α = (diazole in benzene)/(diazole in water), for MeImz = 0.065, and that for *N*-octylimidazole = 20.78.

(28) O. A. El Seoud and F. P. Ribeiro, *J. Org. Chem.*, **41**, 1365 (1976).

(29) The ester concentration in the water pool is expected to decrease as its distribution coefficient α = (ester in benzene)/(ester in water) increases. The values of α increase as the chain length increases; thus, for *p*-nitrophenyl acetate, octanoate, and dodecanoate α = 294, 557, and 605.

(30) Concentrations AOT = 0.1 M, NPA = 9×10^{-5} M, and imidazole = 0.072 M; solvent CH_2Cl_2. Due to the absorption of AOT in the range studied, the reference cell contained 0.1 M AOT solution.

(31) This result is similar to that observed for the imidazole-catalyzed NPA reaction in water. The mechanism can be depicted as follows:



where ROH is the phenol. In case of RImz, the intermediate acetyldiazolium ion would not be expected to attain an experimentally measurable value because it cannot be stabilized by loss of a proton. For details see ref 24.

Additionally, substrate–micelle association is weak due to the absence of H bonding.[32] This, in turn, leads to decreased reagent concentrations in the AOT micellar core, which further decreases the rate. In the absence of strong substrate–micelle interactions, simple partitioning of the reactants between benzene and micelle-solubilized water plays an important role. Based on our bulk partitioning experiments.[27,29] an increase in the water concentration should affect the solubilized ester and MeImz concentrations in opposite directions. The results in Table III indicate that the determining factor is apparently the increased concentration of MeImz in the water pool.

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Registry No. *n*-Butylamine, 109-73-9; *n*-octylamine, 111-86-4; *n*-dodecylamine, 124-22-1; *n*-hexadecylamine, 143-27-1; *N*-methylimidazole, 616-47-7; *N*-butylimidazole, 4316-42-1; *N*-octylimidazole, 21252-69-7; *N*-dodecylimidazole, 4303-67-7; *N*-hexadecylamine, 58175-55-6; *p*-nitrophenyl acetate, 830-03-5; *p*-nitrophenyl butyrate, 2635-84-9; *p*-nitrophenyl octanoate, 1956-10-1; *p*-nitrophenyl dodecanoate, 1956-11-2; *p*-nitrophenyl hexadecanoate, 1492-30-4; imidazole sodium salt, 5587-42-8; methyl bromide, 74-83-9; butyl bromide, 109-65-9; octyl bromide, 111-83-1; dodecyl bromide, 143-15-7; hexadecyl bromide, 112-82-3; *p*-nitrophenol, 100-02-7; acetic acid, 64-19-7; butyric acid, 107-92-6; octanoic acid, 124-07-2; dodecanoic acid, 143-07-7; hexadecanoic acid, 57-10-3.

(32) ^{1}H NMR studies showed clearly the importance of H bonding for strong substrate–micelle association.[28,33]

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Amination of Ester Enolates with *O*-(2,4-Dinitrophenyl)hydroxylamine

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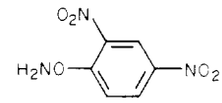
The enolates derived from diethyl malonate and its 2-substituted analogues aminate in good yield with *O*-(2,4-dinitrophenyl)hydroxylamine (1) as an amino-transfer reagent. The 2-aminomalonates thus produced are readily converted to the corresponding amino acids by hydrolysis and decarboxylation. As the ester enolates become more basic, less amino-group transfer is observed, although the aminating reagent 1 is converted to 2,4-dinitrophenol in nearly quantitative yield and starting ester can be recovered with excellent material balance. It is shown that the destruction of 1 in part involves the formation of diimide, diagnosed by the hydrogenation of added alkenes. Direct reaction of 1 with NaH and KH also lead to destruction of 1 and the isolation of 2,4-dinitrophenol, but without detection of diimide and with formation of ammonia. The reaction with KH resulted in a detonation. The mechanisms of the various processes are considered.

The introduction of amino nitrogen into organic molecules is generally accomplished by using the nucleophilic capabilities of nitrogen. Among methods of this type are the Gabriel synthesis, alkylation of tertiary amines with alkyl halides, and the formation and subsequent reduction of Schiff bases, all of which may be justifiably regarded as classical. One can, however, contemplate the reversal of the usual polarity of nitrogen and carbon in order that an amino group might be introduced as an electrophile using a carbon nucleophile, in the sense of eq 1. Despite

$$\geq C:^- + \text{“}^+NH_2\text{”} \rightarrow \geq CNH_2 \qquad (1)$$

the potential utility of an approach of this sort, there are few ways to accomplish this conversion. If the carbanion to be aminated has no α-hydrogen, *p*-toluenesulfonyl azide can be used to transfer the azido group to carbon; this can be subsequently reduced to the amine.[1] The nitroso group can be transferred to carbon by using isoamyl nitrite or related reagents; again, subsequent reduction is necessary to achieve the desired amine functionality.[2]

The family of reagents H_2NX, where X is a leaving group, is attractive as a potential NH_2^+ synthon. Receiving the greatest attention among reagents of this sort are the commercially available hydroxylamine-*O*-sulfonic acid (X = OSO_3H), *O*-mesitylenesulfonylhydroxylamine, and *O*-(2,4-dinitrophenyl)hydroxylamine, 1. In particular, ex-



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tensive use of these compounds to aminate amines,[3] amide anions,[4] sulfides,[3,5] and sulfoxides[6] has been reported. It is somewhat surprising, however, that reports of amination of carbanions are rather sparse. Sheradsky et al.[7] reported the amination of 9-carbethoxyfluorene in benzene/CH_3OH/$KOCH_3$ in 50% yield and the amination of diethyl phenylmalonate in dimethylformamide/NaH in 53%

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