N-(2-Chloro-3,3-dimethylbutyl)chloroacetamide (1b): 83%; mp 84 °C; IR ($CHCl_3$) 3420, 1680, 1535 cm^{-1}; exact mass calcd for $C_8H_{15}Cl_2NO$ 211.0522, found 211.0525. Anal. Calcd C, 45.29; H, 7.13; N, 6.60; Cl, 33.42. Found: C, 45.50; H, 7.18; N, 6.49; Cl, 34.02.

N-(2-Chloro-3,3-dimethylbutyl)trichloroacetamide (1c): 95%; mp 85 °C; IR ($CHCl_3$) 3425, 1720, 1515 cm^{-1}; exact mass calcd for $C_8H_{13}Cl_4NO$ 278.9751, found 278.9755. Anal. Calcd C, 34.19; H, 4.66; N, 4.98; Cl, 50.46. Found: C, 34.95; H, 4.85; N, 4.87; Cl, 49.10.

N-(2-Chloro-3,3-dimethylbutyl)trifluoroacetamide (1d): 98%: mp 65 °C; IR ($CHCl_3$) 3440, 1735, 1550 cm^{-1}; exact mass calcd for $C_4H_5F_3ClNO$ ($M^+ - C_4H_8$[12]) 175.0012, found 175.0016. Anal. Calcd for $C_8H_{13}F_3ClNO$: C, 41.48; H, 5.66; N, 6.04; Cl, 15.30. Found: C, 41.27; H, 5.90; N, 5.92; Cl, 15.08.

Ethyl N-(2-Chloro-3,3-dimethylbutyl)carbamate (1e): 75%; mp 69 °C; IR ($CHCl_3$) 3450, 1720, 1520 cm^{-1}; exact mass calcd for $C_9H_{18}ClNO_2$ 207.1022, found 207.1022. Anal. Calcd C, 52.04; H, 8.73; N, 6.79; Cl, 17.07. Found: C, 51.87; H, 8.73; N, 6.91; Cl, 17.30.

N-(2-Bromo-3,3-dimethylbutyl)trichloroacetamide (1f): 98%; mp 83 °C; IR ($CHCl_3$) 3440, 1720, 1518 cm^{-1}; exact mass calcd for $C_8H_{13}Cl_3BrNO$ 322.9246, found 322.9246. Anal. Calcd C, 29.52; H, 4.03; N, 4.30. Found: C, 29.61; H, 4.19; N, 4.18.

N-(2-Chloro-3,3-dimethylbutyl)succinimide (2): 48%;[13] mp 92 °C; IR ($CHCl_3$) 1785, 1720 cm^{-1}; ^1H NMR ($CDCl_3$) 1.07 (s, t-C_4H_9), 2.75 (s, succinimid group), 3.72 (dd, J = 13.4, 2.4 Hz, H_X), 3.93 (dd, J = 13.7, 11.4 Hz, H_M), 4.16 ppm (dd, J = 11.4, 2.4 Hz, H_A); exact mass calcd for $C_{10}H_{16}ClNO_2$ 217.0869, found 217.0867. Anal. Calcd C, 55.17; H, 7.40; N, 6.43; Cl, 16.28. Found: C, 54.94; H, 7.55; N, 6.30; Cl, 16.41.

Acknowledgment. We thank the "Ministère de l'Education du Québec" and the Natural Sciences and Engineering Council of Canada for financial support.

Registry No. 1a, 83269-99-2; 1b, 83270-00-2; 1c, 83270-01-3; 1d, 83270-02-4; 1e, 15044-22-1; 1f, 83270-03-5; 2, 83270-04-6.

(12) The molecular ion could not be detected. In the mass spectra of all the other compounds, the base peak did correspond to the facile loss of C_4H_8 ($M^+ - 56$ fragment).

(13) A yield of 50% is reported in ref 5, but no physical, spectroscopic, and analytical data are given.

Salt Effects on the Decarboxylation of 6-Nitrobenzisoxazole-3-carboxylate Catalyzed by 1-Methyl-4-dodecylpyridinium Iodide Micelles. Effect of Microenvironment vs. Ion Exchange

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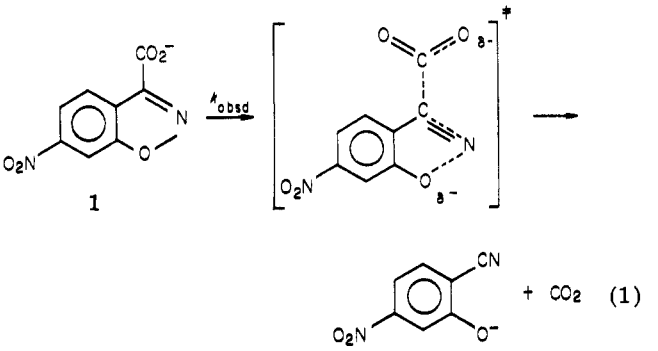
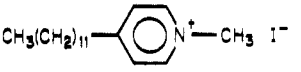
Micellar catalysis of unimolecular reactions is determined by two factors, the binding of the substrate to the micelle and the nature of the reaction medium at the binding sites. These binding sites are usually located in the Stern layer of the micelle.[1,2] One particularly popular and useful model reaction to probe microenvironmental effects is the intermediateless decarboxylation of 6-nitrobenzisoxazole-3-carboxylate (1; eq 1).[3] This reaction is



(1)

remarkably sensitive to solvent effects.[4] Important solvation factors are hydrogen bonding interactions involving the carboxylate group of the substrate and dispersion interactions of the polarizable transition state.

The microenvironment in the Stern layer of micelles has been studied by using a variety of techniques including solubilization of extrinsic micropolarity reporter probes.[5] It is generally found that the local polarity is reduced with respect to bulk water. For ionic amphiphiles this result reflects the presence of the ionic head groups, the counterions, and the nearness of the first part of the hydrocarbon chain. Recent investigations involved 1-methyl-4-dodecylpyridinium iodide (2), an amphiphile carrying



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an *intrinsic* polarity reporter group.[6] From the position of the first long-wavelength intramolecular charge-transfer (CT) absorption band of the head group in the micelle, it could be deduced that the micropolarity in the Stern layer is rather similar to that in ethanol as expressed in Kosower's Z value (Z = 80.6). In the presence of a series of electrolytes, the micropolarity is still further reduced.[6]

In the present study we have employed the decarboxylation of 1 as a kinetic probe for the micropolarity in the Stern layer of micelles formed from 2. Interestingly, in the presence of NaCl, NaBr, and NaI a competition occurs between surface polarity effects and ion exchange.

Results and Discussion

A plot of the first-order rate constants (k_{obsd}, 30 °C) for decarboxylation of 1 as a function of the concentration of the amphiphile 2 is shown in Figure 1. When the concentration of 2 is increased, the value of k_{obsd} gradually reaches a limiting value which is the usual behavior for a micellar-catalyzed unimolecular reaction.[1] Analysis of this plot in terms of the enzyme model for micellar catalysis[7] provides values for the rate constant in the micelle (k_m = 3.42 × 10^{-4} s^{-1}) and for the binding constant of 1 to the micelle (K_S = 1160 M^{-1}). As expected on the basis of the reduced micropolarity in the Stern layer, the rate constant is increased as compared with that in water (k_w = 2.1 × 10^{-6} s^{-1}; k_m/k_w is ca. 160). The rate constant at the micellar surface is of the same order of magnitude as that for decarboxylation in ethanol (k_{EtOH} = 10 × 10^{-4} s^{-1})[4]. This result is in agreement with the respective Z values (vide supra). In addition, the micellar catalysis is of the same

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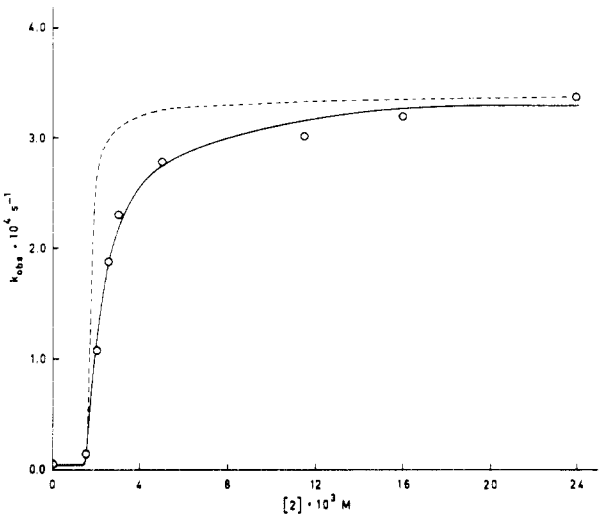

Figure 1. Plot of k_{obsd} for decarboxylation of 1 as a function of [2] at 30.0 °C (○). The solid line was calculated according to the enzyme model (cmc = 1.5×10^{-3} M, $k_m = 3.42 \times 10^{-4}$ s^{-1}, K_S = 1160 M^{-1}) and the dashed line according to the ion-exchange model (cmc = 1.5×10^{-3} M, $k_m = 3.42 \times 10^{-4}$ s^{-1}, $\alpha = 0.15$, $K_{S/I} = 16$).

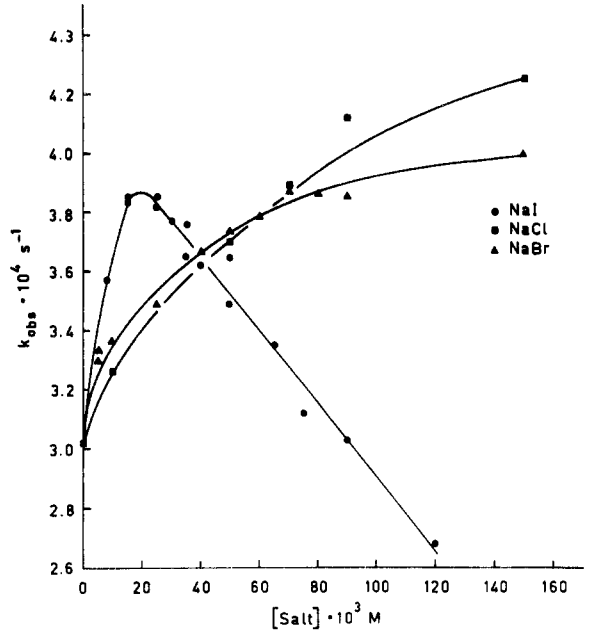

Figure 2. Salt effects on k_{obsd} for decarboxylation of 1 in the presence of micelles of 2 ([2] = 11.5×10^{-3} M).

order of magnitude as that found for some other cationic amphiphiles.[3c]

The effect of varying concentrations of electrolytes (NaCl, NaBr, NaI) on the rate constant in the micellar pseudophase is shown graphically in Figure 2. Whereas k_{obsd} increases continuously with increasing concentration (from 0 to 160×10^{-3} M) of NaCl and NaBr, there is a maximum for k_{obsd} in the NaI solutions (at ca. 20×10^{-3} M). At still higher concentrations of NaI k_{obsd} becomes smaller and ultimately attains values even smaller than k_{obsd} in the absence of salt. We submit that the salt effects shown in Figure 2 reflect two opposing effects: lowering of the micropolarity in the Stern layer as the result of increased counterion binding[6] and exchange of anionic 1 with the anion of the electrolyte at the micellar surface. For NaI it has been shown that the micropolarity in the Stern layer decreases with increasing concentration of NaI up to about 20×10^{-3} M of NaI and then remains almost constant ($Z = 78.6 \pm 0.2$)[6]. This fall in micropolarity is accompanied by an increase of k_m (Figure 2). At NaI concentrations beyond ca. 20×10^{-3} replacement of substrate molecules by iodide anions in the Stern layer becomes the dominant factor and more and more of the substrate is forced to react in the aqueous pseudophase. The contribution of ion exchange can be further analyzed by evaluating the substrate–iodide exchange constant $K_{S/I}$ according to the ion-exchange model proposed by Quina and Chaimovich.[8] This constant can be obtained by solving eq 2 in which S_T and S_b are the total and micel-

$$K_{S/I} = \frac{S_b}{S_T - S_b}\left(\frac{\alpha C_D + \text{cmc} + S_b + [\text{NaI}]_T}{(1-\alpha)C_D - S_b}\right) \quad (2)$$

lar-bound concentrations of substrate (S), respectively, C_D is the concentration of micellized amphiphile, cmc is the critical micelle concentration, α is the degree of ionization of the micellized amphiphile, and $[\text{NaI}]_T$ is the total concentration of sodium iodide. The effects of NaI on α and the cmc have been determined previously,[6] and these data have been employed in our treatment. As expected, the kinetically determined cmc (1.5×10^{-3} M, 30 °C) was slightly different from that obtained from optical absorption spectroscopy ($2.45 \pm 0.05 \times 10^{-3}$ M, 25 °C). The first value was employed in the kinetic analyses. Its variation with [NaI] was set equal to that measured in the earlier work.[6] This leaves S_b as the sole unknown parameter in eq 2. Returning to the enzyme model, one can write

$$k_{obsd}S_T = k_mS_b + k_w(S_T - S_b) \quad (3)$$

Rewriting gives

$$S_b = \frac{k_{obsd} - k_w}{k_m - k_w} S_T \quad (4)$$

and S_b can be calculated if k_m is known.

Since the micropolarity in the Stern layer of the micelles is constant beyond [NaI] = 20×10^{-3} M, we assume that k_m is also constant under these conditions. Extrapolation of the corresponding part of the plot of k_{obsd} vs. [NaI] to [NaI] = 0 leads to $k'_{obsd} = 4.14 \times 10^{-4}$ s^{-1}, a value which is free of ion-exchange effects. Since the salt effects have been measured at [2] = 11.5×10^{-3} M and K_S = 1160 M^{-1} (vide supra), 92% of the substrate will be bound to the micelles in the absence of added salts. Thus

$$0.92(k_m - k_w) = k'_{obsd} - k_w \quad (5)$$

and we find $k_m = 4.5 \times 10^{-4}$ s^{-1} ([NaI] > 20×10^{-3} M). Substitution of k_m in eq 4 gives S_b, and then eq 2 provides $K_{S/I} = 16 \pm 2$. Using this ion-exchange constant, the plot of k_{obds} vs. [2] has been reproduced (Figure 1). In view of the assumptions involved in the kinetic analysis,[8] the correspondence is satisfactory. With changing [NaI], the variation of $K_{S/I}$ stays within the experimental error in this quantity. This is remarkable since added salts are known[5] to influence the aggregation number (and thus the packing of the amphiphiles in the aggregate), the degree of ionization, and, at higher salt concentrations, the shape of the micelle. Apparently, in the concentration range studied, the response of substrate and iodide binding to these effects is rather similar despite the different nature of both anions.

In the case of added NaCl and NaBr no maximum in k_{obsd} is observed (Figure 2). At low salt concentrations, the salt effects follow the sequence NaI > NaBr > NaCl in accordance with the known abilities of the salts to decrease the micropolarity.[6] Unfortunately, the data do not

(8) Quina, F. H.; Chaimovich, H. *J. Phys. Chem.* **1979**, *83*, 1844.

permit a reliable dissection of the overall salt effect into contributions of micropolarity and ion-exchange effects.

Experimental Section

Materials. 6-Nitrobenzisoxazole-3-carboxylic acid was prepared according to the methode of Borsche[9] and Lindemann and Cissee.[10] The product was crystallized from methanol; mp 149–159 °C (lit.[11] mp 167–169 °C, monohydrate). A phenol test[11] was negative. 1-Methyl-4-dodecylpyridinium iodide (**2**) was kindly provided by Dr. E. J. R. Sudhölter[12] (mp 112.5–113 °C, lit.[12] mp 112.5–113 °C). The salts used in all experiments were of the highest grade available (obtained from Baker or Merck AG) and were dried before use over P_2O_5 in vacuo at 100–150 °C for 24 h.

Kinetic Measurements. The formation of 2-cyano-5-nitrophenoxide from **1** was monitored at 30.0 °C by following the increase of the absorbance at 410 nm with a Beckmann Model 24 spectrophotometer equipped with a thermostated cell holder. The initial concentration of **1** was 1.2×10^{-4} M. All solutions contained 2×10^{-3} M of NaOH. For improvement of the reproducibility, a stream of nitrogen was led through the NaOH solution before **1** and **2** were added. In all cases satisfactory first-order kinetics were observed, the rate constants (obtained by Guggenheim's method) were reproducible to within 2%. Data plots in terms of eq 2 and 3 were analyzed by using an HP-25 programmable calculator.

Acknowledgment. We are much indebted to B. Eling for performing preliminary kinetic measurements.

Registry No. **1**, 42540-91-0; **2**, 62541-13-3.

Supplementary Material Available: Rate constants for decarboxylation of **1** as a function of the concentration of **2** (Table I) and as a function of the concentration of NaCl, NaBr, and NaI at a fixed concentration of **2** (11.5×10^{-3} M) (Table II) (2 pages). Ordering information is given on any current masthead page.

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New Synthesis of α,β-Unsaturated Aldehydes from Nitro Paraffins

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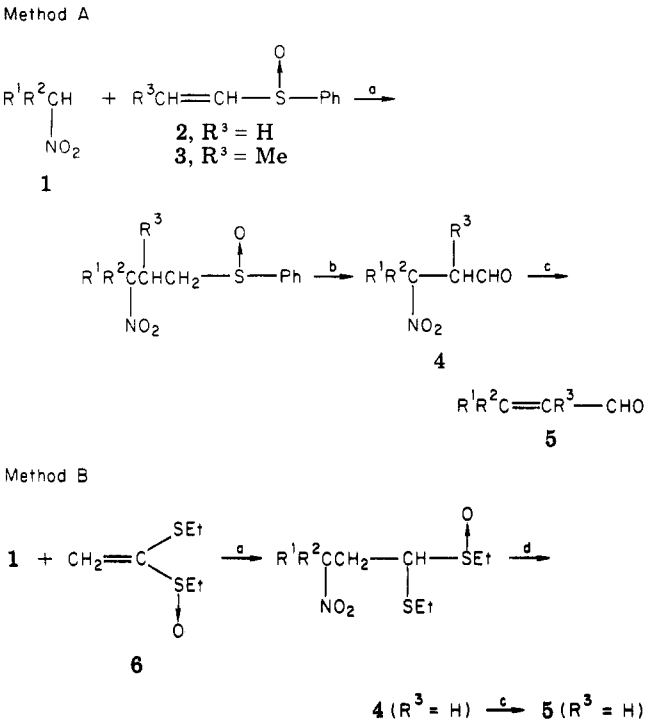
The nitro group has found extensive utility as an activating group in the formation of carbon–carbon bonds, but it generally fails to serve as a leaving group in substitution or elimination reactions by ionic processes.[1] In a special case, if electron-withdrawing groups exist at the β-position of the nitro function, elimination of nitrous acid takes place readily to give olefins in good yields.[2] So, if simple methods can be devised to convert nitro paraffins (**1**) to β-nitro aldehydes (**4**), a new synthetic method to get α,β-unsaturated aldehydes (**5**) from **1** is possible. In this paper we report the realization of this conversion via the Michael addition of **1** to α,β-unsaturated sulfoxides.

Scheme I[a]



[a] (a) DBU/CH_3CN, room temperature, 24–48 h; (b) $(CF_3CO)_2O$, aqueous $NaHCO_3$; (c) DBU/Et_2O, room temperature, 3 h; (d) $HClO_4$ (70%).

The methods are summarized in the generalized equations in Scheme I. As a sulfoxide, phenyl vinyl sulfoxide (**2**), phenyl 1-propenyl sulfoxide (**3**), or ketene diethyl dithioacetal *S*-monooxide (**6**) was employed.

The Michael addition of **1** to vinyl sulfoxides required 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a base. The reaction was complete at room temperature in 24–48 h and gave the adduct in quantitative yields. Other bases such as triethylamine, potassium fluoride, and tetramethylguanidine were not so effective as DBU. The adduct was converted to **4** without purification by treatment with trifluoroacetic anhydride (TFAA) followed by hydrolysis with aqueous sodium hydrogen carbonate[3] (method A) or by acid hydrolysis[4] (method B). Elimination of nitrous acid from **4** resulted in the clean formation of **5** in good overall yields. The sulfoxides for method A are more readily obtained than those for method B. However, method B has the following merits. Hydrolysis to get **4** is very simple. Furthermore, the Michael addition of primary nitroalkanes to **6** gave the selective monoadduct, but that to **2** gave a mixture of the mono- and diadducts.

(1) The synthetic utility of aliphatic nitro compounds is well documented: (a) N. Kornblum, *Angew. Chem., Int. Ed. Engl.*, **14**, 734 (1975). (b) D. Seebach, E. W. Colvin, F. Lehr, and T. Weller, *Chimia*, **33**, 1 (1979). (c) N. Ono and A. Kaji, *Yuki Gosei Kagaku Kyokaishi*, **38**, 115 (1980). In these references some reactions use a nitro group as a leaving group. However, nitromethane or nitroethane reacts with p-$MeC_6H_4S^-$, a strong nucleophile, very slowly in DMF to give the substitution product in 80% or 3% yield, respectively. This suggests that nucleophilic substitution of R–NO_2 is very difficult: M. Benn and A. C. M. Meesters, *J. Chem. Soc., Chem. Commun.*, 579 (1977).

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