Experimental Section

Materials.—Diphenylcarbamoylimidazole was prepared by allowing 1 *M* imidazole to react with 0.025 *M* diphenylcarbamoyl chloride in 30% aqueous dioxane at room temperature for 24 hr. Crystals were collected and recrystallized from ethanol, mp 119.3–122.5°, $\nu_{C=O}$ 1695 cm^{-1}. Analysis was performed by Schwarzkopf Analytical Service, Woodside, N. Y. *Anal.* Calcd for $C_{16}H_{13}N_3O$: C, 72.99; H, 4.98; N, 15.96. Found: C, 72.90; H, 4.93; N, 15.68. Diphenylcarbamoyl chloride 1,1-diphenylurea, ethyl diphenylcarbamate, and diphenylamine are from Distillation Products Industries. *p*-Nitrophenyl diphenylcarbamate is from Sigma Chemical Co. Dimethylcarbamoylpyridinium chloride was prepared by the method of Johnson and Rumon.[21] Diphenylcarbamoylpyridinium chloride, mp 107.5–108.5°, was prepared by the method of Herzog.[22] Diphenylcarbamoyl fluoride, mp 81.8–82.0°, was prepared by allowing equimolar KF and diphenylcarbamoylpyridinium chloride to react in 10% acetonitrile, and twice recrystallized from ethanol. This product has the same melting point as the diphenylcarbamoyl fluoride obtained by treatment of diphenylcarbamoyl chloride with SbF_3 in xylene.[5] The mercaptoethanol thiol ester of diphenylcarbamic acid was prepared from the treatment of II, 0.10 *M*, with 0.2 *M* mercaptoethanol, pH 8.0, for 5 min. The product was isolated in 89% yield in the crude form and recrystallized from ethanol, mp 77.5–78.5°. Elemental analysis was performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. *Anal.* Calcd for $C_{15}H_{15}NO_2$: C, 65.91; H, 5.53; N, 5.13; S, 11.71. Found: C, 65.38; H, 5.59; N, 5.03; S, 13.23. The infrared spectrum of this compound (taken with a Beckman IR-4 spectrometer) shows an OH stretching frequency at 3450 cm^{-1}, a carbonyl stretching frequency at 1666 cm^{-1}, and a single carbonyl stretching frequency at 1666 cm^{-1}. The latter frequency is in contrast with the 1724 cm^{-1} frequency of ethyl diphenylcarbamate, and serves to rule out the formation of the isomeric oxygen ester in the reaction. The presence of the OH stretching frequency confirms this structure because the isomeric product would have only a weak band due to SH stretching at *ca.* 2400 cm^{-1}. The thiol ester product absorbs maximally at 241 nm in the uv.

Chemical Kinetics.—The hydrolysis rate of diphenylcarbamoyl chloride, fluoride, -imidazole, and -pyridinium ion was followed by measuring the increase in absorption produced at 280 nm by the diphenylamine product. In case of acetate, phosphate, Tris, and thiol-containing buffers which react directly with diphenylcarbamoylpyridinium to form products which do not rapidly liberate diphenylamine, the disappearance of the substrate was measured by utilizing the ability of carbamoylpyridinium ions to undergo ring-opening reactions which produce chromophoric materials.[20] In this case diphenylcarbamoylpyridinium ion is allowed to react with the desired buffer, and 1-ml aliquots are removed at timed intervals and placed in 5 0-ml portions of 1 *M* NaOH. The absorbances of these solutions are then measured at 422 nm. At this pH the chromophoric material disappears only slowly with a specific rate constant of 0.012 min^{-1}.

The reaction of diphenylcarbamoylpyridinium ion with more basic buffers was followed at 340 or 422 nm, which is a measure of the concurrent ring-opening process. The alkaline hydrolysis of diphenylcarbamoyl chloride was followed at 245 nm in 0.01–1 *M* NaOH. Diphenylcarbamate, λ_{max} 245 nm, is the stable product from this reaction from diphenylcarbamoyl chloride, λ_{max} 227 nm. The reaction of diphenylcarbamate to produce diphenylamine depends only on hydrogen ion and has a specific rate constant $k_H = 0.45 \times 10^8\ M^{-1}\ min^{-1}$ at 25°.[11] The result is that this carbamate is the stable product of diphenylcarbamoyl chloride in alkaline solutions. The alkaline hydrolysis of diphenylcarbamoyl chloride and fluoride and of diphenylcarbamoylimidazole was also followed by a quenching procedure, in which appropriate amounts of 1 *M* acetic acid are added to aliquots from the alkaline reacting solutions. This gives a pH 4–6 solution, depending upon the conditions, in which diphenylcarbamate from the alkaline hydrolysis reaction readily produces diphenylamine which can be monitored at 280 nm. The pK_a of diphenylcarbamoylimidazole was measured by placing known quantities of the substrate in buffers of various pH values and measuring the absorbance of the acid form at 226.5 nm and the basic form of the substrate at 233 nm. The relationship $pK = pH + \log A_u - A/(A - A_i)$ was used, where A_i, A_u, and A are optical absorbances of the fully ionized form the unionized form, and observed form, respectively.

Analysis of Kinetics.—Semilog plots of $A_t - A_\infty$ *vs.* time were made, where the *A*'s refer to the optical absorbances. Good linearity is achieved to past 90% reaction in most cases. The rate constant is calculated from the slope of the line divided by 2.303. The observed rate constants are plotted against the buffer concentration if a series of buffers of constant pH and varying concentration is used. The slope of such a plot is taken as the specific rate constant, k_2, for the interaction of the substrate with the buffer component. The intercept, k_1, is equal to $k_w + k_{OH^-}(OH^-)$, the sum of the water and hydroxide terms. In the case where hydroxide is the variable buffer component k_o refers to the water term, k_w.

Registry No.—1, 83-01-2; 2, 33712-38-8; diphenylcarbamoyl fluoride, 10055-41-1; *p*-nitrophenyl diphenylcarbamate, 3848-46-2; diphenylcarbamoylimidazole, 2875-79-8; mercaptoethanol thiol ester of diphenylcarbamic acid, 33712-42-4.

Acknowledgment.—We wish to thank Mrs. Grace Tan and Mrs. Diana Kibby for carrying out some of the kinetic determination.

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Micellar Effects upon the Decarboxylation of 3-Bromo and 2-Cyano Carboxylate Ions[1]

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The decarboxylation of 2-cyano-2-phenylacetate ion *via* an intermediate carbanion is catalyzed *ca.* 660-fold by micelles of cetyltrimethylammonium bromide, CTABr, but that of 3-bromo-3-phenylpropionate ion *via* an intermediate carbonium ion is retarded by cationic micelles. The micellar-catalyzed decarboxylation of the 2-cyano acetate ion is enhanced by added inorganic salts, but added salts reduce the micellar inhibition of the decarboxylation of the 3-bromo propionate ion.

Decarboxylation of the 6-nitrobenzisoxazole-3-carboxylate ion (I) is strongly catalyzed by cationic micelles of cetyltrimethylammonium bromide (CTABr).[3] This implies that the transition state with its delocalized negative charge interacts more strongly than I with the cationic micelle. We were therefore interested in examining micellar effects upon decarboxylations of other carboxylate ions. Two reactions, having different mechanisms, were examined.

The decarboxylation of 2-cyanocarboxylate ions (II)

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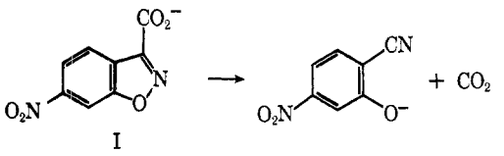
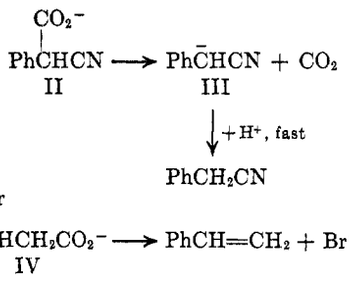
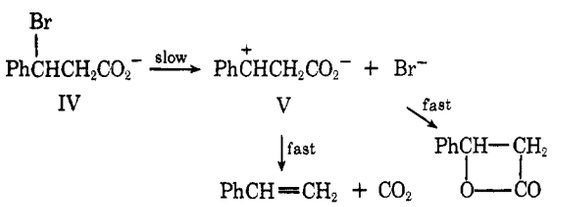
(2) U. S. PHS Postdoctoral Fellow.
(3) C. A. Bunton and M. J. Minch, *Tetrahedron Lett.*, 3881 (1970).



I



involves rate-limiting formation of a resonance-stabilized carbanion (III)[4] and, like the decarboxylation of benzisoxazole carboxylate ions,[5] is much faster in aprotic solvents than in water.[6] On the other hand, Bordwell and his coworkers have shown that the rate-limiting step of the decarboxylation of the 3-bromocarboxylate ion (IV) is ionization to give a carbonium



ion (V) which either decarboxylates or collapses to a lactone.[8]

The solvolysis of similar 2-bromo carboxylate ions also proceeds *via* a carbonium ion.[8a] Such ionizations are not particularly sensitive to changes in the solvent, and the interaction between the carboxylate ion and the carbonium center appears to be electrostatic rather than covalent.

By analogy with other systems we expected that decarboxylation of II would be catalyzed by cationic micelles, but the situation should be more complex for the decarboxylation of IV. Incorporation of the 3-bromo carboxylate ion IV into a cationic micelle will stabilize the initial state and this of itself would reduce the reaction rate, but this inhibition may be offset by interaction between the cationic micelle and both the leaving bromide ion and the organic residue, especially if the latter is lactonelike.

There are many examples of electrolyte inhibition of micellar catalysis.[9,10] This inhibition appeared to be a general phenomenon and was readily explained in terms of competition between a counterion and the ionic reagent for the ionic micelle.[10,11] However, the rate of decarboxylation of I in the presence of micellized CTABr is increased by some salts,[12] and we were interested in finding other examples of this unexpected salt effect. The effectiveness of micelles as catalysts or inhibitors varies widely from one system to another and we are particularly interested in elucidating the factors which control these effects.

Experimental Section

Materials.—The 3-bromo-3-phenylpropionic acid was prepared by saturating a warm solution of cinnamic acid in acetic acid with HBr gas for 2.5 hr. The solvent was removed under reduced pressure on a rotary evaporator to yield the product which, after recrystallization from $CHCl_3$, had mp 139.5–141.5° (lit.[13] mp 137°).

Ethyl 2-cyanophenylacetate was prepared from benzyl cyanide[14] and was saponified by Hessler's method using 1 *M* NaOH.[15] After recrystallization from benzene, 2-cyano-2-phenylacetic acid had mp 69–72° (lit.[4] mp 72–73°). It appears that the compound can exist in more than one crystalline modification, because when the sample was kept at 50° for 3 days the melting point rose to 89–91°. On recrystallization from benzene the melting point went back to 69–72°.

The samples of CTABr and the dicationic surfactants (VI) were prepared and purified by methods already described.[11,16]

$$\text{cetyl}\overset{+}{\text{N}}\text{Me}_2(\text{CH}_2)_n\overset{+}{\text{N}}\text{Me}_2\text{cetyl}\ 2\text{Br}^-$$

VI

(a, b, c: n = 2, 4, 6, respectively)

Kinetics.—The reactions were followed spectrophotometrically using either a Cary 11 or a Gilford spectrophotometer with a water-jacketed cell compartment. The first-order rate constants, k_ψ, are in sec^{-1}.

The relatively rapid decarboxylation of 3-bromo-3-phenylpropionate ion (IV) was followed by introducing the acid, in 5 μl of ether, to 3 ml of aqueous surfactant containing 0.02 *M* NaOH in a cuvette. A perforated Teflon plunger was used to mix the solution rapidly in the cuvette. The substrate concentration was 5×10^{-5} *M*. The reaction was followed at 248 nm.

The decarboxylation of 2-cyano-2-phenylacetate ion (II) is relatively slow at room temperature.[4] An aqueous solution of the acid was added to a solution of CTABr and 1.7×10^{-2} *M* Tris buffer at pH 8; the resulting substrate concentration was $7\text{–}10 \times 10^{-4}$ *M*. The reaction was followed at 235 nm.

The change in absorbance is small for the decarboxylation of the 2-cyanocarboxylate ion (II), and the absorbance of CTABr compounds the problem; consequently, the rate constants have an uncertainty of *ca.* 10%. However, this accuracy is sufficient to establish the magnitude of the micellar catalysis.

Products of Decarboxylation of the 3-Bromo Acid (IV).—The formation of styrene and lactone from 3-bromo-3-phenylpropionate ion has been examined by Bordwell and Knipe.[8] If reaction took place in the micellar phase, the reaction products might change when the reaction mixture contains CTABr. In order to test this possibility we allowed a solution of 2×10^{-4} *M* IV to react at pH 8.1 in water and a second solution to react under the same conditions except that 10^{-2} *M* CTABr was present. After complete reaction, the first solution was also made 10^{-2} *M* in CTABr and it was found that the two mixtures had identical absorbances in the region 210–340 nm, so that there is no marked change of products in the two systems.

Spectral Measurements.—Because of their reactivity we could not examine II and IV in aqueous CTABr and therefore we measured the spectral shifts of the structurally similar 3-phenylpropionate ion, both in aqueous 0.05 *M* CTABr and in ethanol. In water 3-phenylpropionate ion has peaks at 267.2, 263, 257.5, 253.1, and 247.2 nm, the third and fourth peaks being the largest. The changes of wavelength and extinction coefficient of these peaks in CTABr and ethanol are given in Table I.

(4) A. Thomson, *J. Chem. Soc. B*, 1198 (1970).
(5) D. S. Kemp and K. Paul, *J. Amer. Chem. Soc.*, **92**, 2555 (1970).
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(10) E. H. Cordes and R. B. Dunlap, *Accounts Chem. Res.*, **2**, 329 (1969).
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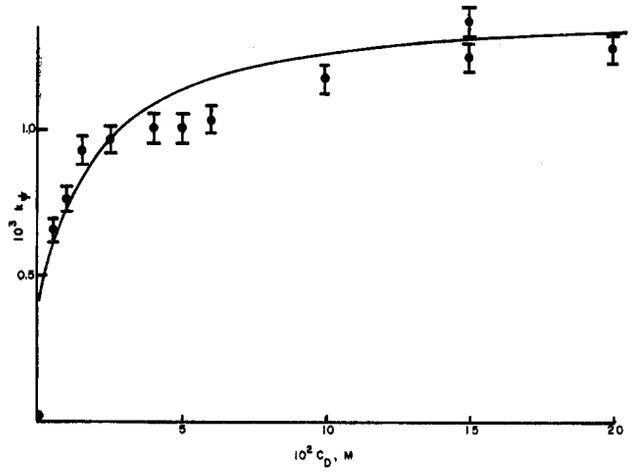

Figure 1.—Catalysis of the decarboxylation of 2-cyano-2-phenyl acetate ion by CTABr at 33.2°.

TABLE I

SPECTRAL SHIFTS OF 3-PHENYLPROPIONATE ION

Medium	Δλ, nm	Δε
0.05 *M* CTABr	+1.5	−25[a]
	+1.8	−7[b]
EtOH	+0.9	−32[a]
	+1.4	−14[b]

[a] Relative to ε 252 at 257.5 nm in water. [b] Relative to ε 248 at 260 nm in water.

These spectral shifts are consistent with incorporation of 3-phenylpropionate ion, and by analogy II and IV, in micellar CTABr (*cf.* ref 9).

Results

Kinetics.—Micelles of CTABr effectively catalyze the decarboxylation of 2-cyano-2-phenylacetate ion (Figure 1 and Table II), but they retard that of 3-bromo-3-phenylpropionate (Figure 2).

Micellar Catalysis.—The variation of k_ψ, for the decarboxylation of II, with CTABr concentration (c_D) shows the typical kinetic form of a spontaneous reaction catalyzed by micelles; that is, k_ψ increases to a plateau value, and then remains constant.[3,11,17] The kinetic forms characterized by a rate maximum rather than a plateau value are very common for bimolecular reactions catalyzed by micelles, suggesting that micellar deactivation of the external reagent is an important factor.[9,11] At lower temperatures the substrate is not soluble enough for accurate rate measurements in the absence of CTABr and the k_ψ values of 9.3×10^{-7} and 3.9×10^{-6} sec^{-1} for 25.0 and 33.2°, respectively, were calculated by extrapolation from $10^4 k_\psi = 1.42$ at 55.5°, 5.55 at 65.0°, and 10.8 at 69.8°. These rate constants gave a linear Arrhenius plot and Thomson's value of $10^4 k_\psi = 2.61$[4] at 60.0° fell on this plot. The activation parameters for reaction in the absence of surfactant are $\Delta H^\pm = 31.5$ kcal mol^{-1} and $\Delta S^\pm = 21$ eu, and are very similar to those for decarboxylation of the *p*-chloro compound.[4]

The activation parameters for decarboxylation catalyzed by 0.15 *M* CTABr are $\Delta H^\pm = 20$ kcal mol^{-1} and $\Delta S^\pm = -8.5$ eu (calculated from the rate constants in Figure 1 and Table II and $k_\psi = 30.6 \times 10^{-4}$ sec^{-1} at 39.9° in 0.15 *M* CTABr). The decrease of $\Delta H^\pm$ and $\Delta S^\pm$ for the micellar-catalyzed decarboxylation is similar to that observed by Cramer and Kampe for cyclodextrin-catalyzed decarboxylation,[7] and is readily explicable in terms of an incorporation of the substrate into the micelle. The maximum rate enhancements [*ca.* 660-fold at 25° and 360-fold at 33.2° based on plateau values of $k_\psi = 6.5 \times 10^{-4}$ sec^{-1} at 25.0° and 1.35×10^{-3} sec^{-1} at 33.2° (Figure 1 and Table II)] by micelles of CTABr are larger than that found for the decarboxylation of 6-nitrobenzisoxazole carboxylate ion.[3]

TABLE II

RATE CONSTANTS FOR THE DECARBOXYLATION OF 2-CYANOPHENYLACETATE ION IN CTABr[a]

$10^2 c_D$, *M*	$10^4 k_\psi$, sec^{-1}
0.0	0.0093
1.0	5.73
5.0	6.03
6.0	5.50
7.5	6.50
9.0	6.33
10.0	6.72
12.5	6.50
15.0	5.45

[a] At 25.0° at pH 8 (0.017 *M* Tris buffer).

TABLE III

SALT EFFECTS UPON THE DECARBOXYLATION OF 2-CYANOPHENYLACETATE ION IN CTABr[a]

Salt	c_{salt}, *M* 0.1	0.2	0.3	0.4	0.5	0.6
Na_2SO_4		1.84		2.22		2.44
NaCl	1.98	2.15		2.37		2.43
KCl	1.82	2.10	2.24			
KH_2PO_4	1.49		1.78	1.74	1.75	1.91
K_2HPO_4	1.70	1.75	1.88	2.17		

[a] Values of $10^3 k_\psi$, sec^{-1}, at 33.2° in 0.15 *M* CTABr; in the absence of added salt $10^3 k_\psi = 1.35$ sec^{-1}.

With some micellar-catalyzed or inhibited reactions it is possible to treat the kinetics in terms of an equilibrium binding of the substrate to the micelle and a rate constant for reaction in the micellar phase.[9,11,17,18] In order to use this approach the micellar concentration has to be greater than that of the substrate, so that a micelle will generally not contain more than one substrate molecule. This condition is not satisfied in our system because the small absorbance change in the reaction together with the absorbance of bromide ions forced us to use relatively high concentrations (*ca.* 10^{-3} *M*) of II.

As expected we find that the anionic surfactant sodium lauryl sulfate had no effect on the rate of decarboxylation of II because II should not be incorporated into an anionic micelle.

Salt Effects on the Micellar-Catalyzed Reaction.—Several added salts were found to increase the rate of decarboxylation of the 2-cyano acetate ion II in the presence of micellized CTABr (Table III). The effects are relatively small but are consistently greater than the experimental uncertainty. Although inorganic phosphate mono- and dianions have smaller effects than sulfate and chloride, the overall effects are not large

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TABLE IV
INHIBITION OF DECARBOXYLATION OF 3-BROMO-3-PHENYLPROPIONATE ION BY CATIONIC SURFACTANTS[a]

$10^4 c_D$, M	Surfactant VIa	VIb	VIc	CTABr
1.0		7.69	6.61	
2.0			2.40	
5.0		3.43		
10.0	5.0	2.83	1.47	14.0
20.0			1.27	10.0
100	2.44			
200	2.38			

[a] Values of $10^2 k_\psi$ at 25.0° in 0.02 M NaOH and 5×10^{-5} M substrate; in the absence of surfactant $10^2 k_\psi = 14.7$ sec^{-1}.

enough to show the marked salt specificity that was observed for the decarboxylation of 6-nitrobenzisoxazole-3-carboxylate ion (I).[12] We were restricted in our choice of salts by the necessity of using only those which did not interfere with the rate measurements by absorbing strongly at 235 nm. We therefore could not use benzoate or tosylate ions which give a marked enhancement of the CTABr micelle-catalyzed decarboxylation of I at salt concentrations comparable to the CTABr concentration and retardation at higher salt concentrations.[12] The decarboxylation of I is catalyzed more by mixed micelles of CTABr and the nonionic detergent Igepal (an aryl polyether) than by micellized CTABr alone, suggesting that a decrease in the charge density of a cationic micelle assists the reaction,[3] but we could not use Igepal in the present work, because it absorbs too strongly at 235 nm. However, similarities between the decarboxylations of I and II suggest that both Igepal and the added salts assist decarboxylation by reducing the charge density of the cationic micelle.[3,12] These interactions between salts and micelles are being examined by nmr and electronic spectroscopy.

Micellar Inhibition.—The kinetic form of the inhibition of the 3-bromo-3-phenylpropionate ion (IV) is very simple (Figure 2). Qualitatively we would expect that there would be no inhibition below the critical micelle concentration (cmc) of CTABr, which is *ca.* 0.8×10^{-3} M.[9] (The cmc is affected by added solutes.) We observe a sharp rate decrease at CTABr concentrations above 1×10^{-3} M, in accord with this simple theory.

It is generally found that inhibiting micelles act by removing the substrate from the aqueous phase, in which it is reactive, into the micellar pseudophase, in which it is less reactive. On this hypothesis the steepness of the plot of k_ψ against c_D should be related to the strength of micelle–substrate binding. This expectation is fulfilled in the present system, where the 3-bromo-3-phenylpropionate ion (IV) should interact strongly with micellar CTABr. Shifts in the uv spectra of 3-phenylpropionate ion in CTABr micelles (Table I) are evidence for such interactions between carboxylate ions and cationic micelles.

Dicationic ammonium salts VI form micelles which are effective catalysts of nucleophilic attack of hydroxide ion upon halonitrobenzenes and hydroxide and fluoride ion upon *p*-nitrophenyldiphenyl phosphate.[16] These micelles are catalytically effective at low surfactant concentration, and we find that they inhibit decarboxylation of IV in low concentration, as is shown in

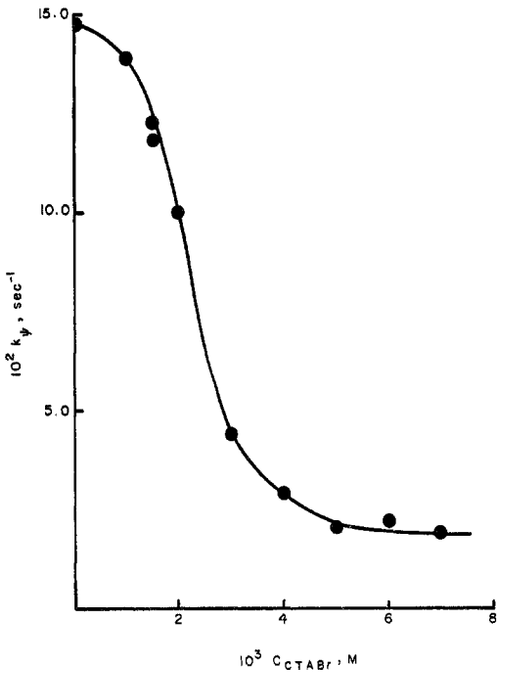

Figure 2.—Inhibition of the decomposition of 3-bromo-3-phenylpropionate ion by CTABr at 25.0°.

Table IV. The surfactant derived from the ethanediamine needed to be in higher concentration than the corresponding butane and hexane derivatives to be an effective inhibitor (*cf.* ref 16).

The values of k_ψ in the presence of relatively high concentrations of either CTABr or VI appear to level out at $k_\psi \approx 2 \times 10^{-2}$ sec^{-1}. At these surfactant concentrations, it can be assumed that the substrate will be wholly incorporated into the micellar pseudophase and that the reaction is therefore not stopped but merely slowed when the substrate is incorporated into a cationic micelle.

Added salts decrease the amount of inhibition by CTABr of the decarboxylation of 3-bromo-3-phenylpropionate ion (Table V). The salt effect is explicable in terms of the partial exclusion of the carboxylate ion IV from micelles of CTABr because of competition for sites on the micelle by added anions; sodium tosylate is especially effective in this role (*cf.* ref 12).

TABLE V
SALT EFFECTS UPON THE MICELLAR-INHIBITED REACTION OF 3-BROMO-3-PHENYLPROPIONATE ION[a]

c_{salt}, M	Salt NaCl	NaOAc	Na_2SO_4	NaTOS
0.01				7.86
0.20	4.50	2.45	3.20	
0.40	4.70	2.63	3.35	
0.60	5.01	3.30	3.30	

[a] Values of $10^2 k_\psi$, sec^{-1} at 25.0° in 0.02 M NaOH and 0.01 M CTABr. In the absence of added salt $10^2 k_\psi = 1.66$ sec^{-1}.

Discussion

Inhibition of Reactions of the 3-Bromo Acid IV.—The inhibition of the decarboxylation of the 3-bromo carboxylate ion IV is readily understandable in terms of Bordwell's mechanistic evidence, which shows that the transition state has considerable zwitterionic

character,[8] because such a transition state (essentially a zwitterion plus a bromide ion) should be considerably destabilized by transfer from water to a micellar pseudophase. On the other hand, if the transition state had considerable lactone character, one might expect the hydrophobic interactions between the micelle and the forming lactone plus those between the cationic micelle and the forming bromide ion to outweigh the energetically beneficial initial state interactions between the carboxylate ion and the cationic micelle so that the rate would not be retarded.

Catalysis of Decarboxylation of the 2-Cyano Acid II. —Although micellar catalysis is often interpreted in terms of a bringing together of reactants in a medium favorable for reaction, some unimolecular reactions are catalyzed by micelles.[3,9,11] Decarboxylations in which a carboxylate ion generates a carbanionlike transition state are strongly catalyzed by cationic micelles. The electrostatic interactions between the cationic micelle and the carboxylate ion assist the incorporation of the latter into the micelle and, of itself, this stabilization of the initial state would result in a rate reduction unless the transition state, with its delocalized negative charge, interacts more strongly with the micelle than the more localized carboxylate ion and offsets this rate reduction. As in the decarboxylation of 6-nitrobenzisoxazole-3-carboxylate ion (I),[3,12] we assume that added salts enhance the CTABr-catalyzed decarboxylation of 2-cyanophenylacetate (II) by reducing the charge density of the micelle. These positive salt effects upon micellar catalysis are unusual and have been observed only for decarboxylations.[12] In all other systems the counterions inhibit catalysis, presumably by excluding an anionic reactant from the micelle.[9-11] Added salts affect micellar structure;[12,19] for example they increase aggregation number, decrease the cmc, and cause the shape of the micelle to change from spherical toward rodlike, but, for all investigated reactions other than decarboxylations, it appears that these structural changes have no direct kinetic effects. For example, in the CTABr-catalyzed hydrolysis of the 2,4-dinitrophenyl phosphate dianion there is almost no increase of rate when the surfactant concentration is increased so much that the micelle becomes rodlike.[17] Decarboxylations appear to be more sensitive to micellar catalysis than most nucleophilic substitutions, where rate enhancements are often only *ca.* 10-fold, and are rarely more than 100-fold,[9,10] as compared with the 660-fold enhancement of the decarboxylation of II at 25°, and probably they are unusually sensitive to the charge density and nature of the micellar surface. When a cyanocarboxylate ion is incorporated into a cationic micelle the negatively charged carboxylate residue will probably be in the water-rich region, where it will suffer electrostatic repulsions if added anions build up in the Stern layer, and added salts should destabilize the initial state. On the other hand, this negative charge becomes delocalized into the carbanionlike transition state where it will be closer to the quaternary ammonium groups of the surfactant and therefore relatively unaffected by anions in the Stern layer.

Registry No.—II, 34220-42-3; IV, 25297-23-8; CTABr, 57-09-0; 3-phenylpropionate ion, 826-17-5.

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Autoxidation of Esters. I. Isobutyl Acetate

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Isobutyl acetate was treated with oxygen in the temperature range 100–120°. This autoxidation reaction seems to proceed as the analogous one with isobutane, but the primary product is, apparently, much less stable. The 2-hydroperoxyisobutyl acetate decomposes to acetone, formaldehyde, and acetic acid at a rate comparable to its rate of formation. In some respects, this decomposition seems not to involve radical intermediates. The formaldehyde is readily oxidized further to formic acid. Carbon monoxide, hydrogen, isobutyric acid, and 2-oxopropyl acetate are minor products in the isobutyl acetate oxidation. The oxidation kinetics conform to the usual free-radical chain mechanism rate expression with little complication.

The reaction of hydrocarbons with oxygen is one of the most thoroughly studied[1] reactions of organic chemistry; yet, the amount of information available on oxygen-containing derivatives is surprisingly small. Aldehydes,[2] ethers,[3] and alcohols[4] are the most closely studied of the oxygen-containing compounds.

Although the oxidation of unsaturated fatty acid esters[5] has been intensively studied, information is lacking on simple esters where the ester function and the oxidatively labile hydrogen are in proximity. In particular, the autoxidative attack on the alcohol portion of an ester at the α and β positions is the major interest here.

$$\overset{\beta}{\mathrm{R}}\overset{\alpha}{\mathrm{CH_2}}\mathrm{CH_2O}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{R'}$$

1

From the few data available in the present literature it appears that trying to investigate oxidative attack

(1) Relatively recent reviews of the subject include L. Reich and S. S. Stivala, "Autoxidation of Hydrocarbons and Polyolefins," Marcel Dekker, New York, N. Y., 1969; F. R. Mayo, *Accounts Chem. Res.*, **1**, 193 (1968); J. Betts, *Quart. Rev., Chem. Soc.*, **25**, 265 (1971).

(2) G. E. Zaikov, J. A. Howard, and K. U. Ingold, *Can. J. Chem.*, **47**, 3017 (1969).

(3) J. A. Howard and K. U. Ingold, *ibid.*, **47**, 3809 (1969); **48**, 873 (1970).

(4) C. F. Cullis and A. Fish in "The Chemistry of the Carbonyl Group," S. Patai, Ed., Interscience, New York, N. Y., 1966, Chapter II, pp 79–186.

(5) W. O. Lundberg, Ed., "Autoxidation and Antioxidants," Interscience, New York, N. Y., 1962. Several chapters deal with fatty acid autoxidation.