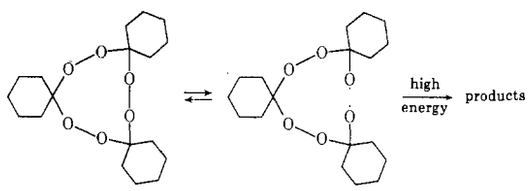
(5) W. O. Ludenberg, "Autoxidation and Autoxidants," Wiley-Interscience, New York, N. Y., 1954.
(6) R. Cubbon, "Progress in Reaction Kinetics," Pergammon Press, New York, N. Y., 1961.
(7) V. L. Antonovskii and V. A. Tereut'ev, *Russ. J. Phys. Chem.*, **39**, 329 (1965).
(8) X. L. Antonovskii and V. A. Terent'ev, *J. Org. Chem. USSR*, **2**, 475 (1966).
(9) V. L. Antonovskii and V. A. Terent'ev, *Russ. J. Phys. Chem.*, **39**, 1549 (1965).
(10) P. R. Story, D. D. Denson, C. E. Bishop, B. C. Clark, Jr., and J. C. Farine, *J. Amer. Chem. Soc.*, **90**, 817 (1968); *Chem. Eng. News*, **46**, 20 (1968).
(11) P. R. Story, B. Lee, C. E. Bishop, D. D. Denson, and P. Busch, *J. Org. Chem.*, **35**, 3059 (1970).
(12) P. R. Story, P. Busch, C. E. Bishop, D. D. Denson, K. Paul, and B. Lee, *Chem. Eng. News*, **48**, 40 (1970).
(13) P. R. Story, and P. Busch, *Synthesis*, 181 (1970).
(14) K. Nozaki and P. D. Bartlett, *J. Amer. Chem. Soc.*, **68**, 1686 (1946); **69**, 2299 (1947).
(15) A. T. Blomquist and A. J. Buselli, *J. Amer. Chem. Soc.*, **73**, 3883 (1951).
(16) E. S. Huyser, and C. J. Bredeweg, *J. Amer. Chem. Soc.*, **86**, 2401 (1964).
(17) W. E. Cass, *J. Amer. Chem. Soc.*, **68**, 1976 (1946); **69**, 500 (1947).
(18) F. R. Mayo, A. Lewis, and C. Walling, *J. Amer. Chem. Soc.*, **70**, 1529 (1948).
(19) C. G. Swain, W. H. Stockmayer, and J. T. Clarke, *J. Amer. Chem. Soc.*, **72**, 5426 (1950).
(20) C. Reichart and K. Dimroth, *Fortschr. Chem. Forsch.*, **2**, 1 (1968).
(21) C. Reichart, *Angew. Chem., Int. Ed. Engl.*, **4**, 29 (1965).
(22) M. G. Alder and J. E. Leffler, *J. Amer. Chem. Soc.*, **76**, 1425 (1954).
(23) E. S. Huyser and R. M. Vanscoy, *J. Org. Chem.*, **33**, 3524 (1968).
(24) E. S. Huyser, "Advances in Free Radical Chemistry," Academic Press, New York, N. Y., 1965.
(25) W. A. Pryor and K. Smith, *J. Amer. Chem. Soc.*, **92**, 5403 (1970).
(26) R. C. Neuman, Jr., *Accounts Chem. Res.*, **5**, 381 (1972).
(27) R. C. Newman, Jr., and E. W. Ertley, *Tetrahedron Lett.*, 1225 (1972).
(28) J. H. Hildebrand and R. L. Scott, "Regular Solutions," Prentice-Hall, Englewood Cliffs, N.J., 1962, pp 88–103.
(29) H. F. Herbrandson and F. R. Neufeld, *J. Org. Chem.*, **31**, 1140 (1966).
(30) J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955).
(31) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, p 394.
(32) R. Criegee, W. Schonenber, and R. Becke, *Ann.Chim. Phys.*, **7**, 565 (1949).
(33) A referee has suggested that a more reasonable estimation of standard deviation would be ±3 kcal for ΔH^*.
(34) A referee has suggested that the high values for the activation parameters may be rationalized thusly.



The high energy process might be rupture of another O–O bond. Some of this might also occur in the decomposition of the dimeric peroxide. A parallel may be found in the decomposition of bis(trifluoromethyl) peroxide in the vapor phase.[35] E_a for this peroxide has been estimated to be 45 kcal/mol. The authors agree that this is a reasonable hypothesis but it still does not explain the large spread in ΔH^* observed for the trimeric peroxide. The rate constants should be determined over a much larger temperature range for the determination of the activation parameters before the mechanism above could be accepted with a modicum of certainty. By determining the rate constants of di-*tert*-butyl peroxide over a large temperature range Walling and Bristol[36] determined values of ΔH^* and ΔS^* which were significantly smaller than those of Huyser and Vanscoy.[23]

(35) J. W. Hogue and J. B. Levy, *J. Phys. Chem.*, **73**, 2834 (1969).
(36) C. Walling and D. Bristol, *J. Org. Chem.*, **36**, 733 (1971).

Micellar Effects upon the Decomposition of 3-Bromo-3-phenylpropionic Acid Effect of Changes in Surfactant Structure[1]

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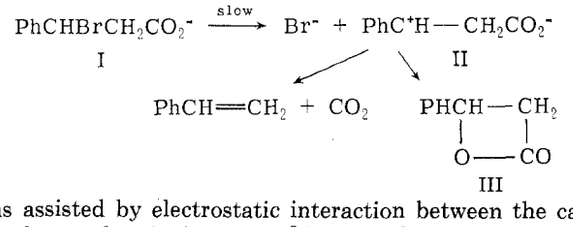
Received June 5, 1974

The SN1 decomposition of 3-bromo-3-phenyl propionate ion is inhibited by cationic micelles of 1-hydroxyethyl-2-dimethylalkylammonium bromide (alkyl = *n*-$C_{12}H_{25}$, *n*-$C_{16}H_{33}$). At high surfactant concentrations an E2 elimination gives *trans*-cinnamate ion in dilute alkali (0.1 *M*). In the absence of surfactant' this E2 elimination is only found in much more concentrated alkali. Zwitterionic micelles of *N,N*-dodecyldimethylalanine and sonicated vesicles (liposomes) of lecithin give small inhibitions and addition of hydrophobic alcohols reduces the surfactant effect.

The solvolysis of 3-bromo-3-phenyl propionate ion (I) in water involves rate limiting formation of the zwitterion (II) which rapidly undergoes both decarboxylation with elimination giving styrene and cyclization giving the β-lactone (III) as a minor product, and it was suggested that reaction



was assisted by electrostatic interaction between the carboxylate and cationic centers.[2] It seemed possible that this interaction would be more effective in a micelle than in water, but micelles of surfactants (detergents) inhibit this and other SN1 reactions[3,4] and the aim of this work was to investigate the effect of changes in the surfactant and solvent and the use of organic solvents which generate reverse micellization. (For reviews of micellar catalysis and inhibition see ref 5–7.) Using a surfactant derived from choline we found formation of *trans*-cinnamate ion by an E2 elimination even in dilute alkali.

Experimental Section

Materials. The preparation and purification of three of the surfactants, CTABr (*n*-$C_{16}H_{33}N^+Me_3Br^-$) and 1-hydroxyethyl-2-dimethylalkylammonium bromides (IVa, R = $C_{12}H_{25}$; IVb, R = $C_{16}H_{33}$), have been described,[8] and the other (V) was prepared by

$RN^+Me_2CH_2CH_2OHBr^-$ (IV) $\quad$ *n*-$C_{12}H_{25}N^+Me_2CHMeCO_2^-$ (V)

standard methods.[9,10] *N,N*-Dimethylalanine was prepared by the reductive methylation of DL-alanine[9] and was quaternized with 1-bromododecane, and the zwitterionic surfactant N,N-dimethyldodecylalanine (V) was recrystallized from acetone. Lecithin (Schwarz Mann, egg white, highly purified) was sonicated at 0° for 5-min periods using a Biosonik IV sonicator to give a clear solution.

The organic solvents were redistilled and the sample of substrate was that used earlier.[3] Redistilled deionized water was used.

Kinetics. The reaction at 25.0° was followed spectrophotometrically at 248 nm using a Gilford spectrophotometer and 5×10^{-5} *M* substrate.[3] The observed first-order rate constants, k_ψ, are in reciprocal seconds.

Table I
Reactions in Mixtures of Water and Alcohols or Glycol[a]

Solvent	H_2O, wt %	10^3 · [surfactant][b]	$10^3 k_\psi$, sec^{-1}
H_2O	100	0.0	147
n-BuOH–H_2O	99.4	0.18[c]	16.8[d]
n-BuOH–H_2O	97.7	0.18[c]	22.2[d]
n-BuOH–H_2O	96.6	0.18[c]	25.9[d]
n-HexOH–H_2O	5	0.0	0.77
n-HexOH–H_2O	5	1.44	1.00
n-HexOH–H_2O	5	12.8	1.21
n-HexOH–H_2O	5	15.6	1.47
n-HexOH–H_2O	5	10.2[e]	1.29
n-HexOH–H_2O	5	15.0[e]	1.27
n-HexOH–H_2O	5	19.5[e]	1.20
Glycol–H_2O	22.5	0.0	13.6
Glycol–H_2O	22.5	1.62	10.5
Glycol–H_2O	22.5	5.44	7.2

[a] At 25.0° with 5×10^{-3} *M* KOH and CTABr unless specified. [b] As mole fraction. [c] Equivalent to 10^{-2} *M*. [d] With 2×10^{-2} *M* CTABr in the absence of butanol $k_\psi \sim 17 \times 10^{-3}$ sec^{-1}.[3] [e] *n*-$C_{12}H_{25}NMe_3Br$.

Products. A solution of 3×10^{-4} *M* 3-bromo-3-phenyl propionate ion was allowed to react at 25° in 300 ml of aqueous 0.2 *M* NaOH and 5×10^{-3} *M* 1-hydroxyethyl-2-hexadecyldimethylammonium bromide (IVb). After reaction the surfactant was precipitated by addition of $NaClO_4$ and the solution after centrifugation was treated with more $NaClO_4$ to test for the removal of the cationic surfactant. The solution was acidified to pH 1 (H_2SO_4) at 0° and was extracted with Et_2O. The organic layer was washed (H_2O) and dried (Na_2SO_4 and then $MgSO_4$). The solvent was removed (rotary evaporator) and the residue in MeOH gave a spot R_f 0.66 (Eastman Si-gel sheet) identical with that of *trans*-cinnamic acid. The identification of *trans*-cinnamic acid was confirmed by uv and ir spectroscopy, with λ_{max} in dilute alkali at 269 nm, and the following peaks in the ir region:[11] 1693 (C=O); 1637 (C=C); 1430 (C–O); 939 cm^{-1} (C–H bond).

The composition of the products under kinetic conditions was determined by comparing the absorbances in the region 240 to 275 nm with those of freshly prepared mixtures of styrene and sodium cinnamate. The contribution of the β-lactone (III) was neglected because it is a minor product,[2,12] and its extinction coefficients in the region examined are much less than those of styrene and *trans*-cinnamate ion.

Reactions in Mixed Solvents. When a long-chain alcohol is added to an aqueous cationic micelle, the micellar structure changes, and reverse micelles form when the water content of the solvent is low,[13] but normal micelles form in ethylene glycol and in its mixtures with water.[14]

In the absence of micelles addition of *n*-hexyl alcohol or ethylene glycol to water decreases the rate of reaction as do other organic solvents (ref 2 and 3 and Table I). In *n*-hexyl alcohol–water (95:5 w/w) the reaction rate is initially increased by addition of surfactants, which probably form reverse micelles, but the effects are small. A normal, but small, rate retardation is found in aqueous ethylene glycol. The inhibition by CTABr in water is decreased by addition of small amounts of *n*-butyl alcohol (Table I) and we note that organic solutes can change micellar structure.[15] Because the rate effects are small, we did not examine these systems in detail, but the small rate increase could indicate that the ionic region of the reverse micelle is more polar than the solvent, whereas the opposite occurs with micelles in water. Dramatic rate effects in reverse micelles have been observed in reactions in which acidic or basic reagents are involved.[16]

Results and Discussion

Micelles of the hydroxyethyl surfactants IVa,b inhibit the reaction of I. The effect of IVb is very similar to that of CTABr[3] (Figure 1; in this figure C_D is the concentration of surfactant, or detergent). Micellar catalysis or inhibition often depends upon the length of the *n*-alkyl group rather than upon the nature of similarly charged head groups. As expected the dodecyl surfactant IVa is a less effective inhibitor than IVb. There is some inhibition below the critical micelle concentration, but this behavior is often observed,[3] probably because of substrate induced micellization.

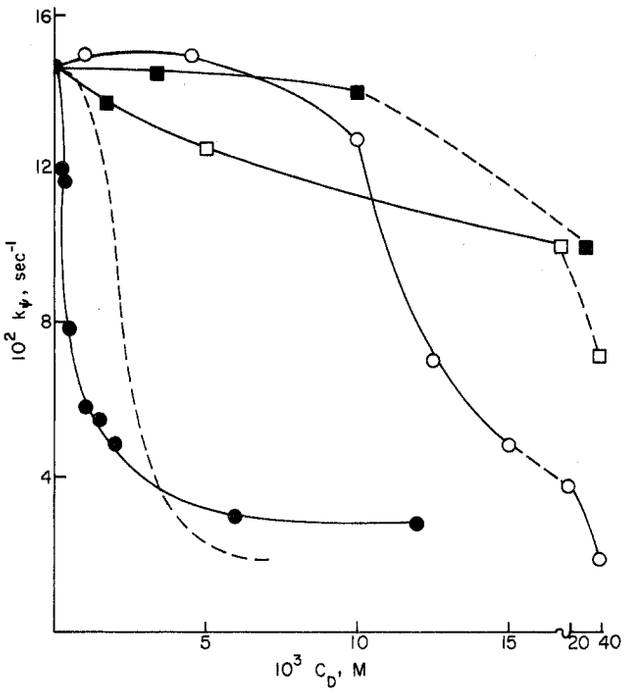


Figure 1. Reaction of 3-bromo-3-phenyl propionate ion in aqueous 0.02 *M* NaOH at 25.0°: ○, IVa; ●, IVb; □, zwitterionic surfactant V; ■, lecithin. The broken line is for reaction in CTABr.[3]

Added salts decrease micellar inhibition of CTABr by screening the cationic micelle from the anionic substrate.[3] Consistently, micelles of the zwitterionic surfactant V are less effective inhibitors than cationic micelles, and this is also true for vesicles (liposomes) of lecithin (Figure 1). (As noted by others, rate measurements in the presence of phospholipids are less accurate than those obtained using synthetic surfactants.[17]) Liposomes effectively catalyze nucleophilic attack upon *N*-alkylpyridinium ions.[17]

Effect of Hydroxide Ion. Micelles of the hydroxyethyl surfactant IV are good nucleophilic reagents at pH high enough for formation of the alkoxide ion VI,[8] and increasing the pH of the solution could increase the reaction rate in three ways. (i) Sodium hydroxide acting as an electrolyte could decrease the inhibition by excluding the substrate from the micelle, *cf.* ref 3. (ii) Zwitterionic micelles of VI might not take up the anionic substrate as readily as do cationic micelles of IV. (iii) Formation of the alkoxide ion VI might introduce a new reaction path.

$$RN^+Me_2CH_2CH_2OH \rightleftharpoons \underset{\text{VI}}{RN^+Me_2CH_2CH_2O^-} + H^+$$

It is not easy to separate these effects because added sodium chloride reduces inhibition by cationic micelles, and the effect (Table II) is very similar to that found with CTABr.[3] However, the hydrophilic hydroxide ion should interact less strongly than chloride ion with a cationic micelle. More important is the relation between rate constant and hydroxide ion concentration (Table III) because k_ψ levels off above approximately 7×10^{-2} *M* sodium hydroxide, suggesting a relation between rate constant and the acid dissociation of IVb. For the acid dissociation of choline $pK_a = 13.9$,[18] and micellization should increase acidity, for example $pK_a \sim 12.4$ for the acid dissociation of micellized IVb, based on assumptions about the validity of the pH

Table II
Effect of Sodium Chloride on the Reaction in Micelles of IVb[a]

C_{NaCl}, M	10^2k_ψ, sec^{-1} [b]	C_{NaCl}, M	10^2k_ψ, sec^{-1} [b]
	2.20	0.15	4.01
0.05	2.55	0.20	4.73
0.10	3.27		

[a] At 25.0° in 6×10^{-3} M IVb and 10^{-2} M NaOH.

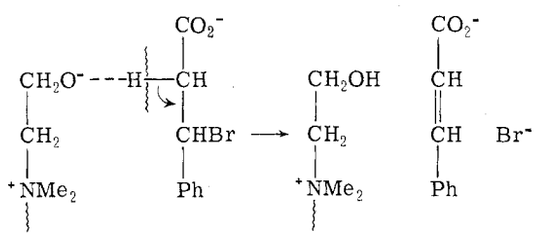
Table III
Effect of Sodium Hydroxide on the Reaction in Micelles of IVb[a]

C_{NaOH}, M	10^2k_ψ, sec^{-1}	C_{NaOH}, M	10^2k_ψ, sec^{-1}
0.0067	2.15	0.050	4.89
0.010	2.20	0.067	5.38
0.020	3.05	0.17	5.48
0.033	4.09		

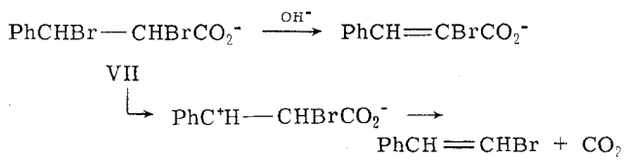
[a] At 25.0° in 6×10^{-3} M IVb.

scale in the presence of micelles (*cf.* ref 19). Thus it seems that formation of the zwitterion VI is important in our system, although because several effects are involved we cannot calculate a pK value from the data in Table III. The main question is whether a new reaction path is being introduced, and evidence on this point comes from a change in the product composition.

In dilute aqueous alkali styrene is formed in an SN1 reaction with β-lactone (III) as a minor product,[2] and added CTABr does not change the product composition.[3] However, even in dilute sodium hydroxide in the presence of the hydroxyethyl surfactant IV *trans*-cinnamate ion becomes the major product (Table IV), suggesting that in approximately 6×10^{-3} M IVb, the SN1 reaction of I is suppressed, but an E2 reaction intervenes,[20] with a micellized alkoxide ion acting as base.



There is precedence for this elimination because α,β-dibromocinnamate ion (VII) in 0.4 M NaOH gives bromocinnamic acid in 45% yield,[22] although in dilute alkali predominant decarboxylation occurs by an SN1 reaction.[2] 3-



Bromo-3-phenyl propionate ion (I) should be a poorer substrate than VII in an E2 reaction, but this reaction is observed in water containing sodium hydroxide in concentration greater than 1 M, as shown in the formation of a small amount of cinnamate ion (Table IV). In support of this hypothesis the first-order rate constant in the absence of surfactant is independent of hydroxide ion up to 1 M and then increases sharply (Table V). This effect of sodium hydroxide is too large to be explained in terms of an electrolyte effect, and the second-order rate constant is 0.08 l. mol^{-1} sec^{-1} in water at 25.0° and neglecting medium effects.

Table IV
Effect of Nucleophilic Micelles on the E2 Reaction of I[a]

C_{NaOH}, M	[Cinnamate], mol %	C_{NaOH}, M	[Cinnamate], mol %
0.05	93[b]	0.1	~0
0.1	97[b]	1.0	11

[a] At 25.0° with 5×10^{-5} M substrate. [b] In the presence of 6×10^{-3} M IVb.

Table V
Effect of Hydroxide Ion on the Decomposition of I in the Absence of Surfactant[a]

C_{NaOH}, M	10^2k_ψ, sec^{-1}	C_{NaOH}, M	10^2k_ψ, sec^{-1}
0.02	14.7	0.50	16.3
0.04	15.6	1.0	17.8
0.06	15.6	2.0	23.7
0.08	15.4	4.0	40.4
0.10	15.2		

[a] In water at 25.0°.

This system is unusual in that micelles of the hydroxy surfactant IV strongly catalyze the E2 elimination which otherwise appears only with high concentrations of hydroxide ion in water, but because they strongly inhibit the normal bromodecarboxylation by an SN1 mechanism they inhibit the overall reaction under all the conditions used.

Registry No.—I, 15463-91-9; IVa (R = $C_{12}H_{25}$), 7009-61-2; IVb (R = $C_{16}H_{33}$), 20317-32-2; V, 52665-42-6; CTABr, 57-09-0; lecithin, 8002-43-5.

References and Notes

(1) Support of this work by the National Science Foundation and the Arthritis and Metabolic Diseases Institute of the USPHS is gratefully acknowledged.
(2) F. G. Bordwell and A. C. Knipe, *J. Org. Chem.*, **35**, 2956, 2959 (1970).
(3) C. A. Bunton, A. Kamego, and M. J. Minch, *J. Org. Chem.*, **37**, 1388 (1972).
(4) C. Lapinte and P. Viout, *Tetrahedron Lett.*, 4221 (1972); 1113 (1973).
(5) E. H. Cordes and R. B. Dunlap, *Accounts Chem. Res.*, **2**, 329 (1969); E. H. Cordes and C. Gitler, *Progr. Bioorganic Chem.*, **2**, 1 (1973).
(6) E. J. Fendler and J. H. Fendler, *Advan. Phys. Org. Chem.*, **8**, 271 (1970).
(7) C. A. Bunton, *Progr. Solid State Chem.*, **8**, 239 (1973).
(9) R. E. Bowman and H. H. Stroud, *J. Chem. Soc.*, 342 (1950).
(10) A. H. Beckett, G. Kirk, and A. S. Virgi, *J. Pharm. Pharmacl, Suppl.*, **11**, 71S (1967).
(11) H. M. Randall, R. G. Fowler, N. Fuson, and J. R. Dangl, "Infrared Determination of Organic Studies," Van Nostrand, New York, N.Y., 1949, p 80; M. St. Ç. Flett, *Spectrochim. Acta*, **18**, 1537 (1962).
(12) S. J. Cristol and W. P. Norris, *J. Amer. Chem. Soc.*, **75**, 632, 2645 (1953); E. Grovenstein and D. E. Lee, *ibid*, **75**, 2639 (1953).
(13) S. Friberg and S. I. Ahmad, *J. Phys. Chem.*, **75**, 2001 (1971); S. I. Ahmad and S. Friberg, *J. Amer. Chem. Soc.*, **94**, 5196 (1972).
(14) A. Ray, *Nature (London)*, **231**, 313 (1971).
(15) M. F. Emerson and A. Holtzer, *J. Phys. Chem.*, **71**, 3320 (1967); J. W. Larsen, L. J. Magid, and V. Payton, *Tetrahedron Lett.*, 2663 (1973); P. Mukerjee and K. J. Mysels, "Critical Micelle Concentrations of Aqueous Surfactant Systems," National Bureau of Standards, Washington, D.C., 1971.
(16) E. J. Fendler, S. A. Chang, J. H. Fendler, R. T. Medary, O. A. El Seoud, and V. A. Woods, "Reaction Kinetics in Micelles," E. H. Cordes, Ed., Plenum Press, New York, N.Y., 1973.
(17) J. Baumrucker, M. Calzadilla, M. Centeno, G. Lehmann, M. Hrdaneta, R. Lindquist, D. Dunham, M. Price, B. Sears, and E. H. Cordes, *J. Amer. Chem. Soc.*, **94**, 8164 (1972).
(18) R. M. C. Dawson, D. C. Elliott, W. H. Elliott, and K. M. Jones "Data for Biochemical Research," Clarendon Press, Oxford, 1959.
(19) C. A. Bunton and B. Wolfe, *J. Amer. Chem. Soc.*, **95**, 3742 (1973).
(20) Description of this reaction as an E2 elimination does not require that C–H and C–Br bond breaking be synchronous. For a discussion of the timing of these steps see ref 21.
(21) F. G. Bordwell, *Accounts Chem. Res.*, **3**, 281 (1970).
(22) T. C. James and J. J. Sudborough, *J. Chem. Soc.*, **95**, 1538 (1909); E. R. Trumbull, R. T. Finn, K. M. Ibne-Rasa, and C. K. Sauers, *J. Org. Chem.*, **27**, 2339 (1962).