alized in terms of steric interactions with a high order of consistency.

Experimental Section

5-Coumaranyllithium was prepared by the addition of n-BuLi (1.9 M, 21 mL, 40 mmol) in hexane to bromocoumaran (8 g, 40 mmol) in ether at 0 °C. The mixture was stirred at 0 °C for 1 h.

2-(5'-Coumaranyl)-endo-norbornanol was prepared by the addition of 5-coumaranyllithium, prepared as described earlier, to norbornanone (3.85 g, 35 mmol) in ether at 0 °C. The reaction mixture was left overnight at room temperature. After the usual workup and removal of solvent, 2-(5'-coumaranyl)-endo-norbornanol was obtained as a colorless solid. It was recrystallized from hexane to give a colorless crystalline solid, mp 75–76 °C.

Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.26; H, 7.83. Found: C, 78.01; H, 7.62.

2-(5'-Coumaranyl)-endo-norbornyl p-nitrobenzoate was prepared by treating the endo alcohol with n-BuLi and then with p-nitrobenzoyl chloride in the usual manner,[25] mp 115–116 °C dec.

Anal. Calcd for $C_{22}H_{21}O_5N$: C, 69.66; H, 5.54; N, 3.69. Found: C, 69.56; H, 5.50; N, 3.52.

2-(5'-Coumaranyl)-exo-norbornanol. The endo alcohol was converted into the chloride by treating with dry HCl gas in methylene chloride at 0 °C in an automatic hydrochlorinator.[26] Solvent was pumped off, and the chloride was hydrolyzed in 60% aqueous acetone at 0 °C in the presence of 100% excess bicarbonate. After the usual workup and removal of solvent, the exo alcohol was obtained as colorless solid. Following recrystallization from hexane, the melting point was 85–86 °C.

Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.26; H, 7.83. Found: C, 78.10; H, 7.57.

2-(5'-Coumaranyl)-exo-norbornyl benzoate was prepared by treating the alcohol with n-butyllithium followed by benzoyl chloride in THF. After the usual workup, the benzoate was used for the solvolytic work without further purification.

Kinetic Measurements. The method used for determining the rate constants of the p-nitrobenzoates and benzoates is essentially the same as that described earlier.[25] The rates and thermodynamic parameters are listed in Table I.

Solvolysis Product. 2-(5'-Coumaranyl)-endo-norbornyl p-nitrobenzoate (1 mmol) was solvolyzed in 80% aqueous acetone containing a 10% molar excess of sodium acetate at 25 °C. After 10 half-lives, the reaction mixture was worked up in the usual way and the product was analyzed by ^1H NMR.

Registry No.—5-Coumaranyllithium, 68151-00-8; 2-(5'-coumaranyl)-endo-norbornanol, 68151-01-9; 2-(5'-coumaranyl)-exo-nor-

bornanol, 68151-02-0; norbornanone, 497-38-1; 2-(5'-coumaranyl)-exo-norbornyl benzoate, 68151-03-1; 5-bromocoumarin, 38169-99-2.

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Substituent Effects in Micellar Catalysis

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Micellar catalysis with sodium 1-dodecanesulfonate has been demonstrated for the acidic hydrolysis of a series of substituted phenylacetohydroxamic acids. The substrate–micelle association constants for the series of compounds correlates well with the empirical lipophilicity substituent constants, π.

Micellar catalysis of many reactions is well documented.[1] Recently we reported micellar catalysis in hydroxamic acid hydrolysis.[2] Previously the only apparent example of micellar effects on amide-like hydrolyses was the very small effect observed in some acetanilide hydrolyses.[3]

The micellar effects on the hydroxamic acid hydrolysis corresponded to the mechanism[4] of Scheme I, where M and S are micelle and substrate, respectively, and k_o and k_m are the rate constants for product formation outside and within the micelle, respectively. This model leads to the relationship[4]

$$\frac{1}{k_o - k_1} = \frac{1}{k_o - k_m} + \left(\frac{1}{k_o - k_m}\right)\left(\frac{N}{K(C_D - cmc)}\right) \quad (1)$$

in which k_1 is the observed pseudo-first-order rate constant,

Scheme I

$$M + S \rightleftharpoons MS$$

$$\downarrow k_o \qquad \downarrow k_m$$
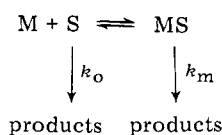
products   products

Table I. Observed Rate Constants[a] for Hydrolysis of Substituted Phenylacetohydroxamic Acids in 0.101 N HCl at 50.1 °C with Sodium 1-Dodecanesulfonate

substituent	registry no.	concn of surfactant[b]							
		0	10^{-3}	0.01	0.02	0.03	0.05	0.07	0.10
none	5330-97-2	1.66	1.58	2.71		5.03	6.30	7.63	8.62
m-CH$_3$	2594-03-8	1.69		4.33	6.89	9.64[c]	11.4	12.9	
p-CH$_3$	2779-74-0	1.75	1.84	5.16		10.2	13.0	14.2	15.4
p-Br	2594-00-5	1.51	1.50	7.59		15.5	18.3	19.6	19.5
p-CH$_3$CH$_2$	68151-27-9	1.79	1.70	8.17	14.3[d]	16.2[e]	18.4	18.9	18.0

[a] Average $10^5 k$, s^{-1}. [b] Molarity, three significant figures, ambient temperature. [c] Surfactant is 0.035 M. [d] Surfactant is 0.024 M. [e] Surfactant is 0.032 M.

Table II. Observed Rate Constants for Hydrolysis of p-Ethylphenylacetohydroxamic Acid in 0.101 N HCl at 50.1 °C with Sodium Dodecylsulfate

surfactant, M[a]	$10^5 k$[b]	surfactant, M[a]	$10^5 k$[b]
0	1.79	0.02	14.1
10^{-4}	1.77	0.03	17.0
10^{-3}	3.36	0.06	17.7
0.01	10.4		

[a] Three significant figures, ambient temperature. [b] Average pseudo-first-order rate constant, s^{-1}.

K is an equilibrium constant, N is the micellar aggregation number, cmc is the critical micelle concentration, and C_D is the total surfactant concentration. Values for K/N and k_m were obtained from the slope and intercept of the excellent linear relationship observed in a graph of the left side of eq 1 vs. $1/(C_D - \text{cmc})$.

Accordingly we have investigated micellar effects upon the hydrolysis of a series of substituted phenylacetohydroxamic acids in order to learn the effects of substituent "hydrophobicity" on K and k_m since the Stern layer is less polar than water[5] and the interior of an aqueous micelle is hydrophobic.[1,5] The hydrophobicity or lipophilicity effects of the substituents can be empirically evaluated by the substituent parameter, π. These values[6] are determined from the logs of the partition coefficients of a series of compounds partitioned in an octanol–water system.

Results and Discussion

The kinetic data are given in Tables I and II. Sodium 1-dodecanesulfonate (Table I) was chosen as the surfactant rather than the previously[2] used sodium dodecylsulfate since the sulfonate is much more stable than the sulfate in aqueous acid. Ethylphenylacetohydroxamic acid was studied with both surfactants for comparison. The results are very similar—see Tables I, II, and III.

The data of Tables I and II were analyzed according to eq 1. Good linear relationships resulted. Values for the parameters in Table III were obtained by least-squares treatment. The cmc was taken as 10^{-3} as before[2] for sodium dodecylsul-

fate and as 10^{-2} for sodium 1-dodecanesulfonate.[7,8]

Rate maxima as a function of surfactant concentration[1] are frequently observed in bimolecular reactions. A rate plateau but not a maximum is predicted by eq 1. A few explanations[5,9] have been suggested for this phenomenon: inhibition by surfactant counterion as surfactant concentration increases, changes in micellar structure as surfactant concentration increases, and partitioning of the second reactant, often a hydrophilic species such as hydrogen ion, between the bulk phase and the micellar phase. The model of Scheme I does not allow for variation in the fraction of hydrophilic reagent in the micellar phase as the surfactant concentration changes. Bunton et al.[10] have recently reported an investigation of the partitioning of hydrogen ions with sodium dodecylsulfate as the surfactant. The change in the fraction of hydrogen ions in the micellar phase as a function of surfactant concentration decreases as the total hydrogen ion concentration increases. On the other hand, the K values for typical organic substrates are quite high.[1] Therefore the fraction of the organic substrate incorporated into the micelle increases more rapidly with increasing surfactant concentration than would the fraction of hydrogen ion incorporated unless the hydrogen ion concentration were quite low. Consequently we can expect eq 1 to hold over a limited range of surfactant concentration in which the various factors which can contribute to its ultimate failure over a larger surfactant concentration range undergo small changes relative to the micellar effect on the reaction.

Since the experimental conditions were identical for the compounds, the value of N will be the same for these compounds; therefore, the micellar binding constant, K, is proportional to the K/N values in Table III. Accordingly eq 2 may be written

$$\log (K/N)_G = \alpha \pi_G + \log (K/N)_H \qquad (2)$$

where π_G is the empirical lipophilicity substituent constant[6] for substituent G and α is a susceptibility constant. A graph of log $(K/N)_G$ vs. π_G yields an excellent correlation: least-squares fit, $\alpha = 0.669$, correlation coefficient 0.9924, F test[11] 0.1%. Thus partitioning of the substrate between the aqueous and micellar environment apparently parallels partitioning between water and octanol. The π parameters may be useful

Table III. Parameters for Micellar Catalysis[a] of Substituted Phenylacetohydroxamic Acid Hydrolysis

substituent	σ^0[b]	π[c]	$10^4 k_m$[d]	K/N	k_m/k_0[e]	C_D range[f]	R[g]
none	0	0	1.11	27.0	6.72	0.03–0.1	0.9925
m-CH$_3$	−0.07	0.56	1.55	59.9	9.15	0.02–0.07	0.9969
p-CH$_3$	−0.12	0.56	1.82	53.3	10.4	0.03–0.10	0.9999
p-Br	0.26	0.86	2.26	98.4	15.0	0.03–0.07	0.9998
p-CH$_3$CH$_2$	−0.13	1.02	2.13	128	12.0	0.024–0.07	0.9978
p-CH$_3$CH$_2$[h]			2.11[h]	89.1[h]	11.8[h]	0.01–0.06	0.9989

[a] Sodium 1-dodecanesulfonate except as noted. [b] Polar substituent parameter, ref 12, see text. [c] Lipophilicity substituent constant, ref 6. [d] s^{-1}. [e] k_0 is the rate constant in the absence of surfactant. [f] Surfactant concentration range used for calculation with eq 1, see text. [g] Correlation coefficient using eq 1. [h] In sodium dodecylsulfate.

measures of substituent effects in this regard.

Log k_o, where k_o is the rate constant in the absence of surfactant, is well correlated by the polar substituent parameter[12] σ^o (different from the ordinary Hammett σ in that σ^o is derived for use with systems in which a saturated group is interposed between the benzene ring and the reaction center). A least-squares fit yields $\rho = -0.175$ with correlation coefficient 0.9820 and F test[11] 1%. This correlation is expected on the basis of earlier results.[13,14]

Log k_m, where k_m is the rate constant for reaction within the micelle, is not correlated by σ^o and is only roughly correlated by π.

Experimental Section

Phenylacetohydroxamic acid and sodium dodecylsulfate have been described previously.[2] The substituted phenylacetohydroxamic acids were prepared according to the general procedure[14] described before. The IR and ^{1}H NMR spectra are consistent with the indicated structures. The acids were crystallized from water or aqueous ethanol. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. p-Methylacetohydroxamic acid, mp 158–159 °C. Anal. Calcd for $C_9H_{11}NO_2$: C, 65.43; H, 6.71; N, 8.48. Found: C, 64.87; H, 6.85; N, 8.30. m-Methylphenylacetohydroxamic acid, mp 127–128 °C. Anal. Calcd for $C_9H_{11}NO_2$: C, 65.43; H, 6.71; N, 8.48. Found: C, 65.58; H, 6.87; N, 8.37. p-Ethylphenylacetohydroxamic acid, mp 164–165 °C. Anal. Calcd for $C_{10}H_{13}NO_2$: C, 67.01; H, 7.31; N, 7.82. Found: C, 67.21; H, 7.41; N, 7.82. p-Bromophenylacetohydroxamic acid, mp 157–158 °C. Anal. Calcd for $C_8H_8BrNO_2$: C, 41.76; H, 3.51; N, 6.09. Found: C, 41.67; H, 3.76; N, 5.79.

Sodium 1-dodecanesulfonate was prepared by reflux of aqueous sodium sulfite with 1-bromododecane.[15] It was purified by two extractions with hot petroleum ether, crystallization from methanol,

followed by two recrystallizations from 95% ethanol. IR and ^{1}H NMR spectra of the surfactant were the same as published spectra.[16] Anal. Calcd for $C_{12}H_{25}SO_3Na$: C, 52.91; H, 9.25; S, 11.77. Found: C, 52.91; H, 9.26; S, 11.89.

The kinetic measurements were obtained by the method used previously.[2]

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Notes

Photochemical Oxidation of Alcohols by Fe^{3+}, Cu^{2+}, and Ag^+ Ions. 2[1]

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Very recently Stenberg[3] reported the photochemical oxidation of aliphatic alcohols by $FeCl_3$. Similar oxidation reactions are also known with ferric perchlorate.[4] We report here, for the first time, that Ag^+ and Cu^{2+} ions can photochemically oxidize alcohols and that these ions are better oxidizing agents than the reported Fe^{3+} ions. We have successfully oxidized aliphatic and aromatic alcohols, cyclic alcohols, and terpene alcohols with these metal ions in very high yields. $K_3Fe(CN)_6$ also oxidizes these alcohols. The reactions with Ag^+ ions are very clean, fast, and convenient for workup. Table I gives the results.

The irradiations were carried out in a Rayonet photochemical reactor using 350-nm lamps under a nitrogen atmosphere in Me_2SO–water mixture. The oxidation does not proceed in the presence of air. Reactions do not proceed in the

dark. The isolated yields of the products range from 78–96%. The products are identified as the corresponding 2,4-dinitrophenyl hydrazone derivatives and are characterized in comparison with the reported melting point. The solvent Me_2SO by itself does not oxidize the alcohols and also does not get itself oxidized. The completion of the reaction in the case of $K_3Fe(CN)_6$ was marked by the formation of an intense blue precipitate (Turnbull's blue) by adding $FeCl_3$; in the case of reactions with Ag^+ ions by the total precipitation of Ag^0 and in the case of Cu^{2+} ions by the formation of a white precipitate. The nature of this white precipitate is not known. However, further studies are planned to determine it. In all these reactions, the completion was also checked by the absence of alcohols in IR and GLC. Stenberg[3] reports a minimum of 5 h of irradiation with $FeCl_3$ whereas Table I shows that even lesser times of exposure to light are sufficient for the total oxidation of alcohols.

Earlier reports of Brealey[5,6] and the recent report of Stenberg[3] both suggest ketyl radicals as intermediates in the photochemical oxidation of alcohols. As our reactions exhibit radical characteristics such as inhibition by oxygen, possibly similar ketyl radicals are involved in these reactions as well. We have questioned ourselves the nature of the excitation process in the Ag^+, Cu^{2+}, and Fe^{3+} ions and the species of photoexcitation, viz., inorganic cation, ion pair, or alcohol–salt complex. We do have some interesting preliminary results to these questions. However, our studies are still in progress and

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