times with solvent, and the volume was made up (to 25, 50, or 100 ml) with additional solvent. After mixing well, the solvent was delivered by means of a pipet into test tubes having a constriction. The test tubes were placed in a Dry Ice–acetone bath and then sealed. The sealed tubes were then placed in a constant-temperature bath and removed at appropriate intervals for analysis. Because the reaction was slow, it was not found necessary to either cool the volumetric flask below room temperature when aliquots were being removed or to take an initial reading at time = 0 min. At appropriate intervals, a sealed tube was removed from the bath, opened, and filtered into a 50-ml flask. The tube was washed several times with solvent and these washings were added to the flask. The combined filtrate and washings were evaporated under vacuum without heating. The oily residue was dissolved in $CDCl_3$ (0.3 ml) and filtered into an nmr tube. This final filtering was necessary to remove the amine hydrobromide which was dissolved in the original solvent.

For each run 8–10 points were obtained for up to 80% completion. The ratio of **2** to **3** remained constant, within experimental error, over the course of the reaction.

Analysis.—The general appearance of the spectrum was observed at a sweep width of 500 Hz, scanning from approximately 400 to 200 Hz. This was necessary so that spinning side bands, which might be near the methine absorption of the halo ketone, could be shifted away be varying the sample spin rate. The methine absorptions of the halo ketone and both amino ketones were recorded at a sweep width of 50 Hz and at a sweep time of 250 or 500 sec. Saturation of absorbances did not occur during integration which was performed at a sweep time of 50 sec. Each of the absorbances was electronically integrated 8 to 12 times, depending upon reproducibility.

The assumption was made that the sum of the concentrations of halo ketone and both amino ketones was a constant and was equal to the initial concentration of halo ketone. In this way, a quantitative internal standard was unnecessary. Furthermore, the actual size of the aliquot taken and the volume to which the sample was made up were not important. The overall rate constants were calculated assuming that 2 equiv of amine are consumed. The following equation was used in these calculations where a_0 = initial concentration of amine, b_0 = initial concentration of halo ketone, and x = amount of reaction or concentration of both products.

$$\frac{1}{(a_0 - 2b_0)} \ln \frac{b_0(a_0 - 2x)}{a_0(b_0 - x)} = (k_1 + k_2)t$$

The individual rate constants k_1 and k_2 were then determined by multiplying the observed rate constant by the fraction of each product obtained.

Registry No.—**1a**, 33224-47-4; **1b**, 15982-14-6; *tert*-butylamine, 75-64-9.

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Secondary Valence Force Catalysis. XIII. Kinetics of the Alkaline Fading of Crystal Violet in the Presence of Cationic Surfactants[1]

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The alkaline fading of crystal violet in aqueous solution at 30° is subject to catalysis by dilute solutions of *n*-alkyltrimethylammonium bromides. Catalytic effectiveness of these surfactants increases markedly with increasing alkyl chain length as judged both by the maximal rate increase elicited and by the surfactant concentration required to elicit the maximum catalysis. The best catalyst studied, octadecyltrimethylammonium bromide, increases the rate constant for the fading reaction 30-fold at a concentration of 0.0003 *M*. The surfactant-dependent reactions are subject to marked inhibition by anions and by the nonionic surfactant dodecyldimethyl phosphine oxide. The effectiveness of the anions as inhibitors increases in the order $F^- < Cl^- < Br^- < N_3^- < NO_3^-$.

During the last several years there have appeared a substantial number of publications dealing with the kinetics of organic reactions in the presence of micelle-forming surfactants. These studies have been recently reviewed.[2,3] Among them, one of the more notable investigations is that of Duynstee and Grunwald concerning the kinetics of fading of triphenylmethyl dyes.[4] These workers observed catalysis of the attack of hydroxide ion on these cationic dyes by cationic surfactants and marked inhibition for the same reaction by anionic surfactants. The attack of water on these dyes was found subject to inhibition by both cationic and anionic dyes. In many respects, this seminal study provided the basis for later ones concerning other reactions. A subsequent study by Ritchie and coworkers, employing surfactant-free media, has extended study of the uncatalyzed reaction to include additional nucleophiles and has clarified some mechanistic details, including the possible importance of solvent reorientation in the activation process for these reactions.[5] Both in light of this new work and in view of gaps in our information concerning the kinetics of the surfactant-catalyzed reactions, additional study seems warranted. Specifically, there is no available information concerning the effects of surfactant concentration, of surfactant structure, or of salts on the reaction kinetics. To provide this information, we have examined the kinetics of attack of hydroxide ion on crystal violet [tris(*p*-dimethylaminophenyl)methyl cation] in the presence of a series of *n*-alkyltrimethylammonium bromides.

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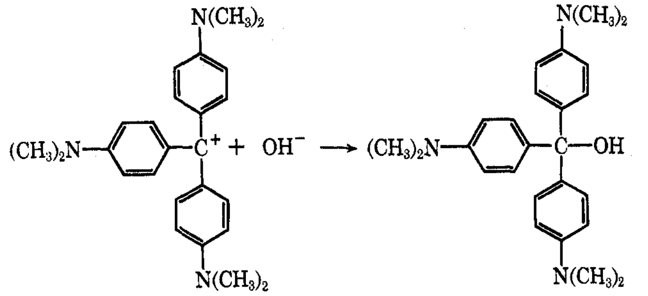

Experimental Section

Materials.—Crystal violet was obtained commercially. *n*-Alkyltrimethylammonium bromides were prepared from carefully redistilled alkyl bromides and trimethylamine according to the method of Scott and Tarter.[6] The surfactants were repeatedly recrystallized prior to use. Dodecyldimethyl phosphine oxide was a gift from the Miami Valley Laboratories of Procter and Gamble, Inc. Reagent grade inorganic salts were obtained commercially. Glass-distilled water was used throughout.

Kinetics.—All rate constants were measured spectrophotometrically employing a Zeiss PMQ II spectrophotometer equipped with a thermostated cell holder. The fading of crystal violet was followed at 590 nm with an initial dye concentration of 2×10^{-6} *M*. First-order rate constants were evaluated from plots of log ($OD - OD_{\infty}$) *vs.* time in the usual way. Excellent first-order behavior was observed in all cases. The reaction proceeded to completion, as judged from the essentially complete fading of the dye at the conclusion of the reaction. All reactions were carried out in aqueous solution at 30° at a concentration of sodium hydroxide of 0.003 *M*.

Results

In the absence of surfactants, the first-order rate constant for fading of crystal violet in 0.003 *M* sodium hydroxide at 30° is 0.040 min^{-1}. This value accords with one calculated from the data of Duynstee and Grunwald at the same base concentration but at 25° of 0.031 min^{-1}.[4] At this base concentration, the fading reaction is almost completely the consequence of attack of hydroxide on the cationic dyes.[4]

In dilute solution of cationic surfactants, the rate of fading of crystal violet is much increased, in accord with the earlier results.[4] First-order rate constants for this reaction in 0.003 *M* sodium hydroxide were measured as a function of the concentration of decyl-, dodecyl-, tetradecyl-, hexadecyl-, and octadecyltrimethylammonium bromides. A portion of the results, those obtained at surfactant concentrations up to 0.01 *M*, are collected in Figure 1. From this data alone, two points are clear: the extent of catalysis increases with increasing chain length and the concentration at which maximal catalysis is observed decreases with increasing chain length. At higher concentrations, catalysis is observed with the decyl and dodecyl surfactants, although the former is only slightly effective. Each rate–concentration profile is qualitatively similar: as the surfactant concentration is increased, the rate constants increase, level off, and then begin to decrease slowly. The rate constant in the presence of 0.01 *M* hexadecyltrimethylammonium bromide and 0.003 *M* hydroxide, 1.1 min^{-1}, is in agreement with one of 0.43 min^{-1} measured under the same conditions except at 25°.[4]

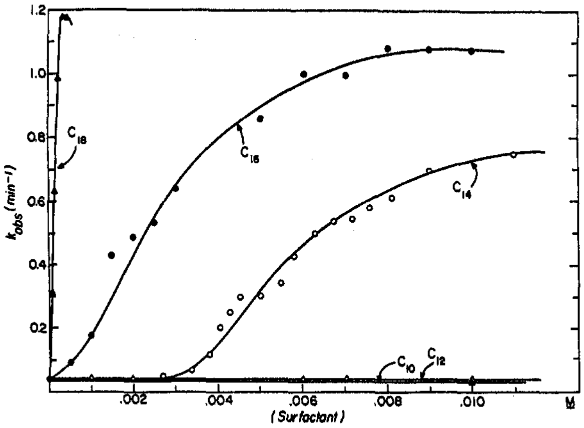

Figure 1.—First-order rate constants for the attack of hydroxide ion on crystal violet in aqueous solution at 30°, (OH^-) = 0.003 *M*, plotted as a function of the concentration of several *n*-alkyltrimethylammonium bromides.

TABLE I

KINETICS OF FADING OF CRYSTAL VIOLET IN 0.003 *M* SODIUM HYDROXIDE IN THE PRESENCE OF A SERIES OF ALKYLTRIMETHYLAMMONIUM BROMIDES AT 30°

Surfactant	Registry no.	k_{max},[a] min^{-1}	k_{max}/k_0,[b]	c_{max},[c] *M*
n-Decyl	2082-84-0	0.075	1.9	0.10
n-Dodecyl	1119-94-4	0.29	5.8	0.028
n-Tetradecyl	1119-97-7	0.75	19	0.011
n-Hexadecyl	57-09-0	1.1	27.5	0.008
n-Octadecyl	1120-02-1	1.2	30	0.0003

[a] Maximum first-order rate constants. [b] Ratio of maximum rate constant to that observed in the absence of catalysts. [c] Concentration of surfactant at which maximal catalysis is observed.

In Table I, the maximal rate increases and the surfactant concentrations necessary to elicit maximal catalysis, taken from the complete set of data, are collected. This data corroborates our conclusions reached above. In Figure 2, the maximal first-order rate constants and the surfactant concentrations required to reach half-maximal catalysis, $(k_{max} - k_0)/2$, an approximate measure of the dissociation constant for the dye–micelle complex, are plotted as a function of the number of carbon atoms in the alkyl chain of the surfactant.

A preliminary study of the fading of malachite green in the presence of the same surfactants gave a pattern of results similar to that just described. The attack of hydroxide ion on this dye, however, is less susceptible to catalysis than is that on crystal violet.

The cationic surfactant-dependent attack of hydroxide ion on crystal violet is sensitive to inhibition by salts. In Figure 3, first-order rate constants for this reaction in the presence of 0.003 *M* sodium hydroxide and 0.01 *M* hexadecyltrimethylammonium bromide are plotted as a function of the concentration of several anions. All are inhibitors. The effectiveness of the anions as inhibitors increases in the order $F^- < Cl^- < Br^- < N_3^- < NO_3^-$. Only the behavior of sulfate is unusual. This ion is an excellent inhibitor at low concentrations but the effect does not increase with increasing concentration above 0.07 *M*. At 0.20 *M* nitrate and azide, the rate constants closely approach those that would have been observed were no surfactant present.

In Figure 4, first-order rate constants for fading of

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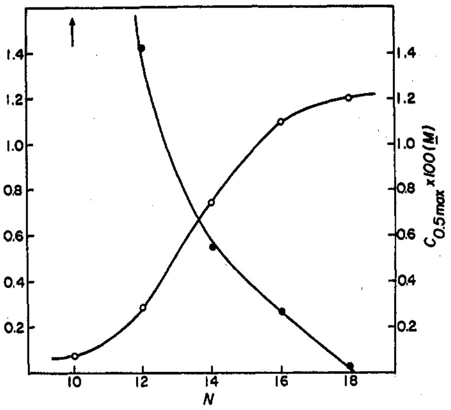

Figure 2.—Plots of the maximal first-order rate constants (left scale, open circles) and the surfactant concentrations required to reach half-maximal catalysis (right scale, closed circles) for the fading of crystal violet as a function of the chain length of *n*-alkyltrimethylammonium bromides.

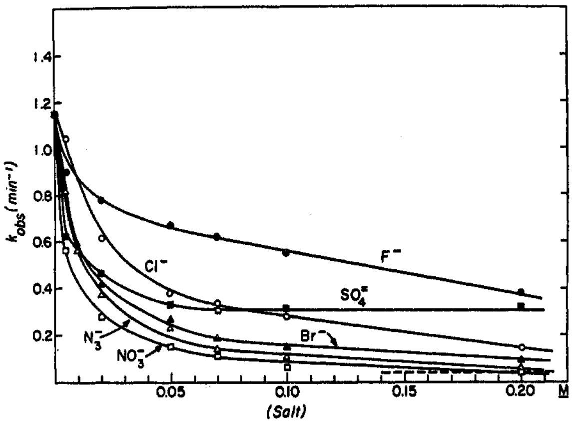

Figure 3.—First-order rate constants for the fading of crystal violet in aqueous solution containing 0.003 *M* sodium hydroxide and 0.01 *M* hexadecyltrimethylammonium bromide at 30° plotted as a function of the concentration of several anions. The dotted line in the lower right of the figure is the rate constant under these conditions in the absence of surfactant.

crystal violet in 0.003 *M* sodium hydroxide and 0.01 *M* hexadecyltrimethylammonium bromide are plotted as a function of the concentration of dodecyldimethyl phosphine oxide. This nonionic surfactant is a potent inhibitor; a concentration of 0.01 *M* nearly suffices to halve the observed catalysis.

Discussion

The catalysis of attack of hydroxide ion on crystal violet and other cationic dyes by cationic surfactants is almost certainly partially the result of electrostatic factors: one expects less electrostatic destabilization for the zwitterionic transition state than for the cationic ground state by the cationic micellar surface. In addition both medium effects and changes in hydrophobic interactions between substrate and micelle as the geometry of the dye changes in approaching the transition state may make significant contributions to the observed rate effects.

Perhaps the most striking aspect of the catalysis of the attack of hydroxide ion on crystal violet by *n*-alkyltrimethylammonium ions is the dependence of the catalysis on the length of the alkyl chain (Figures 1, 2; Table I). Increasingly effective catalysis with increasing surfactant hydrophobicity has been observed several times previously: for the attack of hydroxide ion on *p*-nitrophenyl hexanoate catalyzed by cationic surfactants,[7] the addition of cyanide ion to pyridinium ions catalyzed by cationic surfactants,[8] the hydrolysis of methyl orthobenzoate catalyzed by anionic surfactants,[9] the acid-catalyzed hydrolysis of alkyl sulfates,[10] and the attack of *N*-alkylhistidines on phenyl esters,[11] among other examples. The chain length dependence noted in the present case is perhaps the most striking yet observed.

The concentration of surfactant required to elicit maximal catalysis must principally reflect two things: the cmc for the surfactant and the equilibrium constants for absorption of the substrate onto the micelle. The values for the cmc of some of the surfactants used in this study follow:[2] C-12, 1.5×10^{-2} *M;* C-14, 3.5×10^{-3} *M;* C-16, 9.2×10^{-4} *M*. Clearly, these values partially account for the observed results. For example, catalysis by the C-18 surfactant is maximal at a concentration below the cmc of the other surfactants. Even when one corrects for the differences in cmc, however, it is quite clear that the equilibrium constant for absorption of crystal violet onto the micelles increases rapidly with increasing chain length.

Moreover, it appears that the crystal violet itself induces micelle formation. In each case, catalysis of the reaction is observed at concentrations of the surfactants below the critical micelle concentration. For example, catalysis by the C-12 surfactant is half-maximal by the time that the cmc is reached.

Not only is the special catalytic efficiency of the long-chain surfactants manifested in terms of the concentration of surfactant required to elicit maximum catalysis, but in terms of the maximal rate attained (Table I). Thus, even when the substrate is essentially completely associated with micelles, it is more reactive when the micelles are formed from more hydrophobic surfactants. However, the effect appears to be reaching the point of saturation (Figure 2). Similar observations have been observed in two previous cases.[8,11] This behavior may reflect an increasing electrostatic field at the micellar surface, a change in the medium effects at the micellar surface, or direct contributions of hydrophobic interactions to the activation energy.[11] It is difficult to distinguish between those possibilities in the present case. However, the rate effects appear to approach saturation under conditions in which the hydrophobic interactions, as judged by the shape of the rate-concentration profiles, are still increasing substantially. This suggests that the last of these possibilities may not be very important.

The surfactant-dependent fading of crystal violet is strongly inhibited by anions (Figure 3). The order of effectiveness of anions as inhibitors parallels the expected affinity of the anions for the micellar surface as judged from their relative abilities to lower the cmc and increase the aggregation numbers for these

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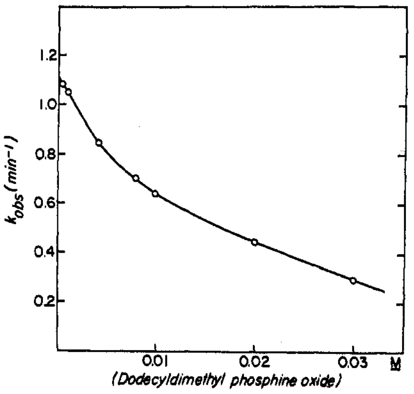

Figure 4.—First-order rate constants for the fading of crystal violet in aqueous solution containing 0.003 *M* sodium hydroxide and 0.01 *M* hexadecyltrimethylammonium bromide at 30° plotted as a function of the concentration of dodecyldimethyl phosphine oxide.

surfactants,[12-14] cause phase separation in solutions of cationic surfactants,[15] associate with strong base anion exchange resins,[16] ion pair with tetraalkylammonium ions in water,[17-19] inhibit carbonic anhydrase,[20] and associate with bilayers containing hexadecyltrimethylammonium bromide.[21] Consequently, this behavior must principally reflect a diminution in the electrostatic field at the micellar surface and, perhaps, specific competition with hydroxide ions for binding sites within the Stern layer. The salt effects observed almost exactly parallel those previously observed for the hydrolysis of *p*-nitrophenyl hexanoate in the presence of the same surfactants,[7] and are related to those observed for the addition of hydroxide ion to 2,4-dinitrochlorobenzene.[22]

The nonionic surfactant dodecyldimethyl phosphine oxide is also an excellent inhibitor for the surfactant-dependent reaction (Figure 4). A similar effect has been noted upon the addition of nonionic species to systems composed of methyl orthobenzoate and sodium dodecyl sulfate.[23] While a number of explanations are possible, the most obvious one is a diminution in the strength of the electrostatic field at the micelle surface due to dilution of the number of charged groups there.

Among earlier studies of surfactant-dependent reactions, this one is most closely associated with catalysis of addition of cyanide ion to pyridinium ions.[8,24] Both reactions involve addition of anions to positively charged substrates and both are subject to catalysis by cationic surfactants. Qualitatively the systems behave in quite a similar way. Quantitatively, however, some differences do appear. The addition of cyanide ion to pyridinium ions is more susceptible to catalysis, less susceptible to inhibition by salts, and more sensitive to the hydrophobicity of the surfactant in terms of maximal rate constants than is addition of hydroxide ion to crystal violet. These observations indicate that the two reactions are differentially influenced by the variety of forces that contribute to relative rates of reactions in purely aqueous solution and in aqueous solutions containing ionic surfactants.

Registry No.—Crystal violet, 14426-25-6; dodecyldimethyl phosphine oxide, 871-95-4.

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