fone was refluxed for a short period of time. It exhibited after distillation only very slightly less rotation (about 0.01°) than that of the above sample. The infrared spectrum of the *d*-sulfone is essentially indistinguishable from that of the *dl*-compound.

Anal. Calcd. for $C_{10}H_{14}O_2S$: C, 60.57; H, 7.12. Found: C, 60.74; H, 7.02.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF FLORIDA STATE UNIVERSITY]

Organic Reactions Occurring in or on Micelles. I. Reaction Rate Studies of the Alkaline Fading of Triphenylmethane Dyes and Sulfonphthalein Indicators in the Presence of Detergent Salts[1]

BY E. F. J. DUYNSTEE AND ERNEST GRUNWALD

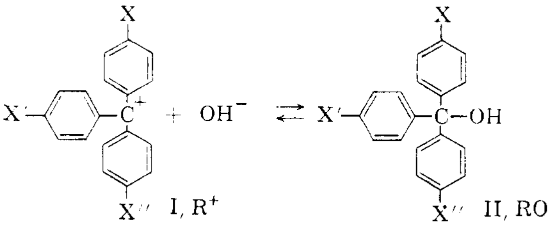
RECEIVED FEBRUARY 4, 1959

The rate of fading of triphenylmethane dyes (R^+, for example crystal violet) and of sulfonphthalein indicators (R^-, for example brom phenol blue) has been measured in alkaline solution in the presence of micelle-forming detergent salts. The rate of fading of R^+ is greatly accelerated by the addition of the cationic detergent, cetyltrimethylammonium bromide, and is greatly retarded by the anionic detergent, sodium lauryl sulfate. The rate of fading of R^- is virtually unchanged when sodium lauryl sulfate is added, but R^- is protected from fading in the presence of cetyltrimethylammonium bromide. Further evidence concerning possible short-range interactions between the micelles and the dye ions has been obtained from the position of the visible absorption band of the dye ions. There is a red shift whenever the charge of the micelles is opposite to that of the dye ions; but there is no significant shift when the two charge types are the same. For the systems investigated, there is a perfect parallelism between the observed effects of detergent salts on the rates of fading and their effects on the position of final equilibrium, as predicted from G. S. Hartley's rules.[10]

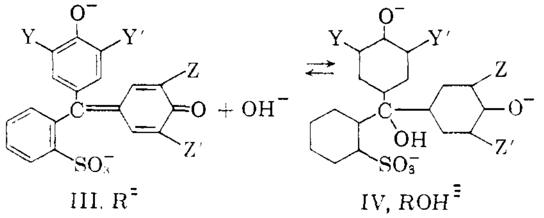
There are theoretical as well as practical reasons for the study of reactivity in the presence of micelles. On the practical side, industrial recipes for carrying out reactions often involve the solubilization of a reactant, a well-known example being emulsion polymerization.[2-4] On the theoretical side, reactions occurring in or on micelles are of especial interest when *ionic* reactants are involved, because of the large electrostatic contributions to the free energy of activation resulting from the micellar charges. Judging by kinetic data for ionic reactions on monolayers,[3,5] the electrostatic acceleration or retardation could easily amount to several orders of magnitude.

In addition, one would expect kinetic "medium effects" due to short-range interactions between the molecules which form the micelles and the molecules of reactant and transition state. These effects could be quite important; for example, it has been shown that the cations of the cationic dye, pinacyanol, are actually incorporated in micelles of opposite charge.[6]

We now report kinetic and equilibrium studies in the presence of micelle-forming salts for reactions of two different charge types: the fading in alkaline solution of triphenylmethane dyes (reaction 1) and of sulfonphthalein indicators (reaction 2). Rates and equilibrium constants for reactions such as 1 and 2 are already available for several dyes in aqueous solution not containing micelle-forming salts.[7,8] The kinetic data in water[7,8] are consistent with these rate laws for the



I, R^+ II, ROH   (1)



III, R^- IV, $ROH^{=}$ (2)

forward reactions (fading)

reaction 1: rate $= k_1(R^+) + k_2(R^+)(OH^-)$ (3)

reaction 2: rate $= k_2'(R^-)(OH^-)$ (4)

Results and Discussion

Pseudo-first order rate constants for the alkaline fading of several dyes at a suitable constant *p*H are listed in Table I. The rate constants were measured in the presence of the cationic detergent, cetyltrimethylammonium bromide (CTABr), of the anionic detergent, sodium lauryl sulfate (NaLS), and in the absence of detergent. In the experiments with added detergent, the concentration of the latter was well above the critical micelle concentration.

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[1] Work supported by the Office of Naval Research. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] F. A. Bovey, I. M. Kolthoff, A. I. Medalia and E. J. Meehan, "Emulsion Polymerization," Interscience Publishers, Inc., New York, N. Y., 1955.

[3] J. T. Davies, in "Advances in Catalysis," Vol. VI, Academic Press, Inc., New York, N. Y., 1954, pp. 1-65.

[4] H. B. Klevens, *Chem. Revs.*, **47**, 1 (1950).

[5] E. Rideal, *Proc. Roy. Soc.* (*London*), **A209**, 431 (1951).

[6] P. Mukerjee and K. J. Mysels, THIS JOURNAL, **77**, 2937 (1955).

[7] R. J. Goldacre and J. N. Phillips, *J. Chem. Soc.*, 1724 (1949).

[8] E. E. Sager, A. A. Maryott and M. R. Schooley, THIS JOURNAL, **70**, 732 (1948), and previous work referred to in this paper.

TABLE I

PSEUDO-FIRST ORDER RATE CONSTANTS AT APPROXIMATELY 25° FOR THE FADING OF 10^{-5} *M* DYES IN WATER

Dye	Substituents	*p*H	10^4k, sec.$^{-1}$ No detergent	 0.01 *M* CTABr[a]	 0.01 *M* NaLS[b]
		Triphenylmethane dyes (R^+)			
Crystal violet	X, X′, X″ = $N(CH_3)_2$	12.00	17	240	~1
Malachite green	X = H; X′, X″ = $N(CH_3)_2$	10.2	8.1	70	1.8
Brilliant green[c]	X = H; X′, X″ = $N(C_2H_5)_2$	10.2	5.1	93	..[d]
		12.16	90	Too fast to measure	1.2
Rosaniline	X, X′, X″ = NH_2; 3-CH_3	10.2	13	16	3.0
		Sulfonphthalein indicators ($R^=$)			
Brom phenol blue	Y, Y′, Z, Z′ = Br	13.00	0.92	No change in *O.D* after 37 hr.	0.85
Brom phenol red	Y, Z = H; Y′, Z′ = Br	13.00	0.11	No change in *O.D.* after 21 hr.	0.11

[a] Cetyltrimethylammonium bromide. [b] Sodium lauryl sulfate. [c] Sample of dye suspected of being slightly impure. [d] Decrease in *O.D.* is too small to permit measurement of rate constant.

The effects of the detergent salts on the reaction rates vary enormously with the charge type of the detergent and of the dye. For the triphenylmethane dyes, the effects are very large—much larger than typical "normal" salt effects. The cationic detergent accelerates the reaction, and the anionic detergent retards it. In the absence of detergent, and in the presence of CTABr, the fading of color is virtually complete; in the presence of NaLS, a measurable amount of dye is left unreacted in the final equilibrium state.

On the other hand, the reaction rate of the sulfonphthalein indicators is *not* affected significantly by the addition of NaLS. The addition of CTABr protects the indicators from fading, but it is not possible to tell from these experiments whether the protection results from a large decrease in the rate of fading, from a large shift in the equilibrium, or from a combination of the two. In the absence of detergent and in the presence of NaLS, the color fading goes virtually to completion at *p*H 13. The completeness of the fading in the absence of detergent is consistent with previous data.[8]

In the cases where the salt effects are large, one would expect that most of the dye is adsorbed on, or incorporated in, the micelles. Additional evidence for such interactions may be obtained from the absorption spectra of these systems. As shown in Table II, there is a significant red shift of the maximum of the visible absorption band whenever the charge of the micelles is opposite to that of the dye ions. On the other hand, there is no significant shift when the two charge types are the same.

TABLE II

EFFECT OF DETERGENTS ON THE POSITION OF THE MAXIMUM OF THE VISIBLE ABSORPTION BANDS IN AQUEOUS SOLUTION

Dye	λ_{max} (mμ) at 10^{-5} *M* concn. No detergent	 0.01 *M* NaLS	 0.01 *M* CTABr
Crystal violet	592	595	592
Brilliant green[a]	630	633	630
Malachite green	620	625	620
Rosaniline	543	548	543
Brom phenol blue	592	592	605
Brom phenol red	574	574	586

[a] Sample of dye suspected of being slightly impure.

The data indicate that there is definitely some interaction when the micelles and dye ions are of opposite charge. We believe that the dye ions are actually being incorporated in the oppositely charged micelles, partly because the observed red shifts are consistent with a change from an aqueous to a hydrocarbon medium—at least for the triphenylmethane dyes,[9] and partly because such an interpretation is consistent with the work of Mukerjee and Mysels.[6] On the other hand, when the charge type of the micelles and of the dye ions is the same, the absence of a shift does not necessarily imply the absence of short-range interactions.

Because of the frequent parallelism between the effect on reaction rates and on equilibria caused by a change in the reaction medium, it is of interest to inquire whether such parallelism exists in our systems. The effect of detergent salts on equilibria involving acid–base indicators may be predicted for each charge type, using a set of rules proposed by Hartley.[10] Thus for reaction 1, which is of the charge type ($+ \rightarrow 0$), the equilibrium is expected to shift to the right (favoring ROH) when cation micelles are added; we find that the rate of fading increases. The equilibrium shifts to the left (favoring R^+) when anion micelles are added; we find that the rate of fading decreases.

For reaction 2, which is of the charge type ($= \rightarrow \equiv$), we would predict from Hartley's rules[10] that the addition of anion micelles has no effect on the equilibrium; we find that the rate of fading is unchanged. Unfortunately, the rules do not permit a clear-cut prediction of the effect of cation micelles; and our own data (Table I) are ambiguous in this case.

It will be noted that in the three cases where comparisons can be made, there is perfect parallelism between the effect of micelle-forming salts on the position of equilibrium and on the rate of the reaction. Since it is implicit in Hartley's rules (which emphasize charge types) that the effect of the micelles on the position of equilibrium is largely electrostatic in origin, we may infer that the effect of the micelles on the reaction rate is also predominantly an electrostatic one. If this view is

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(9) G. N. Lewis, T. T. Magel and D. Lipkin, THIS JOURNAL, **64**, 1774 (1942).

(10) G. S. Hartley, *Trans. Faraday Soc.*, **30**, 444 (1934).

correct, then it is a sufficient condition for the two effects to run parallel that the activation process is of the same charge type as the over-all equilibrium. It is of interest to note that in the present case, the second-order terms involving R^+ (or R^-) and OH^- in equations 3 and 4 are indeed of the same charge type as the corresponding equilibria.

To the best of our knowledge, the only previous kinetic study which is relevant from this point of view is that of the reaction of thiosulfate ion with bromoacetate ion in the presence of anion micelle-forming salts.[11] The ions involved in this reaction are not as large and polarizable as the dye ions used in our studies, so that short-range interactions with the micelles need not be so important, but in any case the charge type of this reaction is such that anion micelles should have no abnormal effect. And, in fact, the effect of the micelle-producing salts on the rate is nearly the same as that of "normal" salts.[11]

Experimental Part

Materials.—Malachite green (oxalate), rosaniline hydrochloride and crystal violet were commercial products of reagent grade. Brilliant green was a commercial product of technical grade and may have been slightly impure.

Sodium lauryl sulfate (U.S.P., from City Chemical Corp., N. Y.) was further purified: 50 g. of NaLS was dissolved in 700 ml. of 95% alcohol and heated. After filtration and cooling, white blades were obtained, which were again recrystallized from 95% ethanol. The final product was dried in the vacuum desiccator.

Cetyltrimethylammonium bromide (technical grade, from Eastman Kodak Co.) was further purified according to the method reported by Mysels.[12] The solid technical product was shaken with anhydrous ether, filtered, and dissolved in a minimum amount of hot methanol. Cooling in the refrigerator gave a crystalline mass which dissolved partly when it was filtered at room temperature. The moist crystal mass which was left on the filter funnel was redissolved in methanol; after addition of anhydrous ether and warming to dissolve all the CTABr, the solution was cooled and a white crystalline product was obtained, m.p. 227–235° dec.

Solutions and Measurements.—The solutions of *p*H 12.00 and 13.00 were prepared from the appropriate amounts of carbonate-free saturated sodium hydroxide and doubly distilled water. The solutions of *p*H 10.2 contained 0.05 *M* boric acid–sodium borate buffer; the *p*H was measured with a Beckman model GS *p*H meter.

The rates of fading were measured by following the optical density of the solutions at the maximum of the visible absorption band of the dyes, using a Beckman model DU spectrophotometer and 1-cm. quartz cells. Plots of $\log (OD - OD_\infty)$ *vs.* time were linear within experimental error. The pseudo-first order rate constants for the fading were obtained from the slopes of these linear plots.

The values of $(OD)_\infty$ were either zero or appreciably smaller than $(OD)_0$, except in the experiments involving the sulfonphthalein indicators in the presence of CTABr.

It was shown in separate experiments that the slow saponification of the detergent salts at *p*H 12 and 13 caused no complications.

TALLAHASSEE, FLA.

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[11] J. A. Erikson and C. A. Lingafelter, *J. Colloid Sci.*, **10**, 71 (1955).

[12] Reference 6, page 2938.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF FLORIDA STATE UNIVERSITY]

Organic Reactions Occurring in or on Micelles. II. Kinetic and Thermodynamic Analysis of the Alkaline Fading of Triphenylmethane Dyes in the Presence of Detergent Salts[1]

BY E. F. J. DUYNSTEE AND ERNEST GRUNWALD

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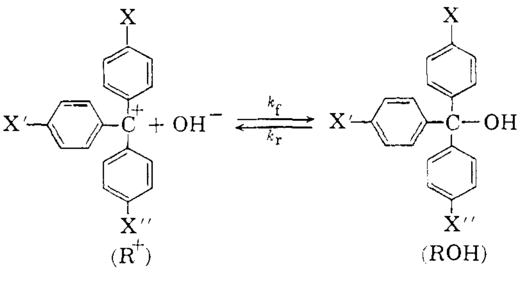
In water, the alkaline fading of triphenylmethane dyes proceeds either by a first-order process (k_1), or by a second-order process with hydroxide ion (k_2). It is shown by means of measurements of solubility, equilibrium constants, or from the rate itself that in the presence of 0.01 *M* cetyltrimethylammonium bromide or sodium lauryl sulfate, the major part of the fading takes place in the micelle phase rather than in the bulk phase. It is inferred, from the nice constancy of the equilibrium constant in the presence of sodium lauryl sulfate, that the electrochemical state of the micelles is reasonably constant when the aqueous phase contains 0.05 *M* boric acid–sodium borate buffer in the *p*H range 9.5 to 11.5, and that kinetic data may be analyzed by classical methods. On this basis it is found that k_1 is depressed somewhat by both detergents, although more so by the anionic one. On the other hand, k_2 is considerably greater in the presence of the cationic detergent (which attracts OH^-) than in the bulk phase, and it is very much smaller in the presence of the anionic detergent than in the bulk phase. Theoretical implications and practical applications of these findings are discussed.

Previous kinetic data[2] for the alkaline fading of triphenylmethane dyes (reaction 1) in the *p*H range 9–13 have been consistent with the rate law shown in equation 2. Moreover, it has been found that the reaction rate is very sensitive to the addition of detergent salts at concentrations that are well above the critical micelle concentration; 0.01 *M* cetyltrimethylammonium bromide (CTABr) accelerated the rate by factors ranging from 1.2 to 18; and 0.01 *M* sodium lauryl sulfate (NaLS) retarded it by factors ranging from 1/4 to 1/75.[3] It is the purpose of this paper to evaluate the effect of the detergent salts on the actual *rate constants* for the fading of crystal violet, malachite green and rosaniline.



(1)

$$rate = k_1 (R^+) + k_2 (R^+)(OH^-) \tag{2}$$

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[1] Work supported by the Office of Naval Research. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] R. J. Goldacre and J. N. Phillips, *J. Chem. Soc.*, 1724 (1949).

[3] E. F. J. Duynstee and E. Grunwald, THIS JOURNAL, **81**, 4540 (1959).