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

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

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 pH 12.00 and 13.00 were prepared from the appropriate amounts of carbonate-free saturated sodium hydroxide and doubly distilled water. The solutions of pH 10.2 contained 0.05 M boric acid–sodium borate buffer; the pH was measured with a Beckman model GS pH 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 $(OD - OD∞)$ 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 $(OD)∞$ 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 pH 12 and 13 caused no complications.
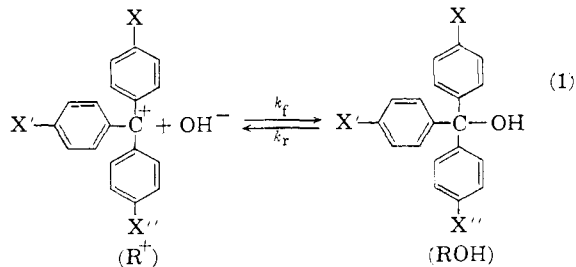
TALLAHASSEE, FLA.

(12) Reference 6, page 2938.

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

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 pH 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 pH 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

(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).

$$rate = k_1 (R^+) + k_2 (R^+)(OH^-) \qquad (2)$$

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.

First it must be shown that the large changes in reaction rate due to CTABr and NaLS are *not* "normal" ionic strength effects. In the rate law as given by equation 2, the second-order process involves the neutralization of ionic charge; hence one would predict a retardation with increasing ionic strength. In the first-order process (which presumably involves attack by a water molecule) the charge of R^+, which is diffuse due to resonance in the ground state, becomes more concentrated in the transition state; hence one would expect a slight increase in rate with increasing ionic strength.

It is possible to estimate the magnitude of the ionic strength effect for our experimental conditions. The ionic strength of the buffers before addition of detergent is in the range of 0.01 to 0.1 M. The addition of 0.01 M detergent increases this value by perhaps 0.02 M. (We assume that the average micelle consists of a hundred large organic ions, and that it binds approximately eighty small counter ions.[4]) Upon applying the Debye–Hückel limiting law to estimate activity coefficients, it is found that the decrease in k_2 caused by an 0.02 M increase in ionic strength should not exceed 20%. The percentage increase in k_1 should be even smaller. Thus the much larger observed effects due to the detergent salts must be ascribed to something other than normal long-range ionic strength effects.

On account of their relatively high molecular weight and large polarizability, one would expect that the dye ions are adsorbed or absorbed to an appreciable extent by the micelles, and there is some spectral evidence to this effect at least in the case of sodium lauryl sulfate.[3] If the portion of the dye which exists in the micelle phase were unreactive, then the addition of detergent should result in a proportionate lowering of the rate. Since in the presence of CTABr the rate is actually accelerated, we may conclude that a sizable fraction of the reaction takes place in or on the micelles. It will be shown in a later section that the same is true also in the presence of NaLS, even though the rate is retarded.

We are therefore faced with the problem of deducing rate constants for reactions which take place largely in or on the micelles. Our study necessarily requires that we change the pH of the bulk phase. But in doing so, we run the risk that the attendant changes in the electrolyte make-up of the bulk phase will cause changes in the size and structure of the micelles and in the potential difference across the double layer surrounding the micelle. These changes in the micelles will in turn cause changes in the reaction rate, in addition to those produced by the change in the hydroxide concentration. Since the two effects cannot be separated, one may justifiably wonder whether the kinetic data obtained in the presence of micelles can be analyzed by classical kinetic methods.

In coping with this problem, we found it helpful to use the equilibrium constant for reaction 1 as an indicator of possible changes in the nature of the micelles. For example, if the concentration of the given detergent salt is kept constant as the pH of the bulk phase is varied, the quantity $(ROH)/(R^+)(OH)^-$ may or may not remain constant, depending on the magnitude of the accompanying changes in the micelles. If we make the plausible assumption that the rate constants are *not a great deal* more sensitive to possible changes in the micelles than the equilibrium constant, then classical kinetic laws will apply to any series of buffer systems in which the quantity $(ROH)/(R^+)(OH^-)$ for the over-all equilibrium remains reasonably constant.

The preceding discussion assumes, of course, that the fraction of the dye which is adsorbed or incorporated by the micelles may be regarded as a dilute solute in the micelle phase. For our experimental conditions, this assumption is probably justified. The formal concentration of the detergent salts was kept constant at 0.01 M, and the dye concentrations were 10^{-5} M or less. If the actual micelles consist of about a hundred detergent ions,[4,5] then the molar concentration of the micelles is of the order of 10^{-4}. This means that there are ten or more micelles for every dye ion, and we may expect that no more than one dye ion will interact with any given micelle. In support of this view, it was found that solutions of triphenylmethane dyes obeyed Beer's law as the concentration of the dye ions was varied up to 10^{-5} M at a constant NaLS concentration of 0.01 M; and that, at a constant dye concentration of 10^{-5} M, doubling the NaLS concentration to 0.02 M had no effect on the optical density. It will be shown that the dye exists almost entirely in the micelle phase under these conditions.

Notation.—We shall use the symbol K to denote the equilibrium constants for reaction 1.

$$K = [ROH]/[R^+][OH^-] \qquad (3)$$

We shall use the symbol k to denote the pseudo-first order rate constants for the approach to equilibrium in a medium of constant pH. In

$$k = (1/t)\,[\ln\,([R_0^+] - [R_\infty^+])/([R_t^+] - [R_\infty^+])] \qquad (4)$$

$$= (1/t)\,[\ln\,(OD_0 - OD_\infty)/(OD_t - OD_\infty)] \qquad (4a)$$

(4a), (OD) is the optical density of R^+ at the maximum of the visible absorption band. In general

$$k = k_f + k_r \qquad (5)$$

where k_f and k_r are the pseudo-first order rate constants for the forward reaction (fading) and the reverse reaction (regeneration of dye from carbinol).

The superscript $\oplus$ will be used to denote quantities measured in the presence of the cationic detergent, CTABr, and the superscript $\ominus$ for quantities measured in the presence of the anionic detergent, NaLS.

Equilibrium Constants.—Values of the equilibrium constant K in water are already available for crystal violet and malachite green.[2] The value of K for rosaniline may be estimated with sufficient

(4) See, for example, J. N. Phillips and K. J. Mysels, *J. Phys. Chem.*, **59**, 325 (1955). The most recent estimate for the average degree of association of 0.01 M NaLS, based on light scattering data, is *ca.* 60 (Mysels and Princen, *ibid.*, in press. We are indebted to Professor Mysels for making these data available to us prior to publication.)

(5) D. Stigter, R. J. Williams and K. J. Mysels, *ibid.*, **59**, 330 (1955).

accuracy from the known value for pararosaniline[2] by means of the ρ–σ linear free relationship.[6]

Equilibrium constants, $K^\ominus$, in the presence of 0.01 M NaLS were defined by the equation

$$K^\ominus = ([ROH]'/[R^+]')/[OH^-] \quad (6)$$

$$= [(OD_0 - OD_\infty)/(OD_\infty)]/[OH^-] \quad (6a)$$

In equation 6, [ROH]' and [R$^+$]' refer to the total concentrations of dye and carbinol, both in the water phase and in the micelle phase, and [OH$^-$] is the hydroxide concentration in the water phase. [ROH]'/[R$^+$]' is equal to $(OD_0 - OD_\infty)/(OD_\infty)$ only if R$^+$ is the only colored species and ROH the only colorless species which are in reversible equilibrium.

The experimental results are summarized in Table I. It is seen that the values of R$^\ominus$ are reason-

TABLE I

EQUILIBRIUM CONSTANTS FOR THE FADING OF TRIPHENYL-METHANE DYES [REACTION 1] WITH AND WITHOUT 0.01 M SODIUM LAURYL SULFATE AT 25°

Buffer	$10^3[OH^-]$, M	$K^\ominus$ (M^{-1})
Malachite green, $K = 12.6 \times 10^5$		
Boric acid–sodium	0.0288	11×10^3
borate 0.05 M^c	.155	14×10^3
	.160	15×10^3
	.182	16×10^3
	Av.	14×10^3
NaOH	10.0	ca. 2000
Crystal violet, $K = 4.4 \times 10^4$		
Boric acid–sodium	2.97	27.6
borate, 0.05 M^c	1.15	23.0
	Av.	25.3
NaOH	19	~7[a]
	19.8	6[b]
	93.2	17[a]
	186	26[b]

$$K^\ominus = 5.2 + 112[OH^-]$$

Rosaniline, $K = 1.9 \times 10^6$

Boric acid–sodium	2.24	232
borate, 0.05 M^c	0.822	211
	Av.	222
NaOH	14.8	55

[a] Dye concentration $<10^{-6}$ M. [b] Dye concentration, 1×10^{-5} M. [c] [OH$^-$] measured with a pH meter.

ably constant in the presence of boric acid–sodium borate buffer over a several-fold variation of [OH$^-$]. The values of $K^\ominus$ obtained in the presence of NaOH are consistently smaller than those obtained in the presence of the buffer, and, judging by the data for crystal violet, vary with the NaOH concentration but not with the dye concentration. The difference between the $K^\ominus$ values measured in the presence of boric acid–sodium borate and those measured in the presence of NaOH may be due to changes in the electrochemical state of the micelles resulting from the change of the electrolyte in the water phase. The variation of $K^\ominus$ with NaOH concentration for crystal violet may also be

(6) The small correction for the 3-CH$_3$ group was made by using $\rho = -3.98$ and $\sigma = 0.041$, as recommended by N. C. Deno and A. Schriesheim, THIS JOURNAL, 77, 3051 (1955).

caused by changes in the micelles or, less probably, by the incursion of a subsidiary equilibrium, such as

$$Ar_3COH + OH^- = Ar_3CO^- + H_2O$$
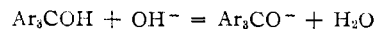
It would appear from these data that, in the pH range 9.5–11.5, 0.05 M boric acid–sodium borate "buffers" are suitable reaction media for the purposes of a kinetic analysis. In this connection, the word "buffer" is written with quotation marks because the pH range 9.5–11.5 brackets the equivalence point in the titration of boric acid with sodium hydroxide, and the buffer capacity is at a minimum. However, since a poor buffer capacity implies that it is possible to change the pH without changing appreciably the electrolyte make-up of the bulk phase, this very feature may be desirable when the principal objective is to maintain the state of the micelles.

Solubility of Carbinols.—It is evident from Table I that the equilibrium for reaction 1 is shifted to the left by the addition of 0.01 M NaLS. Since K exceeds $K^\ominus$ by factors of 1000 or greater, it follows that at least 99.9% of R$^+$ exists in the micelle phase.

We were interested in knowing the distribution between micelle phase and bulk phase more accurately for both R$^+$ and ROH. The carbinols of malachite green and of crystal violet are quite insoluble in water, and it was feasible to measure the extent to which these carbinols are solubilized by 0.01 M NaLS. We actually measured the *ratio* of solubilities, $S_{ROH}^\ominus/S_{ROH}$, in 0.05 M boric acid–sodium borate buffer at pH 10.2, by a spectrophotometric method which is described in the Experimental part. The results are shown in Table II. Owing to the difficulty to achieve good reproducibility in the measurements for the saturated solutions, the results are only semi-quantitative, the accuracy being within a factor of two.

TABLE II

EFFECT OF 0.01 M SODIUM LAURYL SULFATE ON THERMODYNAMIC AND KINETIC QUANTITIES FOR REACTION 1 IN 0.05 M BORIC ACID–SODIUM BORATE BUFFER AT 25°

Ratio	Crystal violet	Malachite green
$K^\ominus/K$	0.0011	0.00058
$k_1^\ominus/k_1$	.086	.37
$k_2^\ominus/k_2$	<.015	<.008
$S_{ROH}^\ominus/S_{ROH}$	6.3	32
$S_{R^+}^\ominus/S_{R^+}$	5700	55,000
Transition states		
$(S_1^\ominus/S_1)^\ddagger$	490	20,000
$(S_2^\ominus/S_2)^\ddagger$	<85	<440

Since $S_{ROH}^\ominus$ is the *total* solubility in both the micelle phase and the bulk phase, the distribution ratio between the two phases is equal to $[(S_{ROH}^\ominus/S_{ROH}) - 1]$.

The analogous ratios $S_{R^+}^\ominus/S_{R^+}$ have been computed by means of equation 7 and are also listed in Table II. It is seen that the major part of ROH, and virtually all of R$^+$, exists in the micelle phase.

$$\frac{S_{ROH}^\ominus/S_{ROH}}{S_{R^+}^\ominus/S_{R^+}} = \frac{K^\ominus}{K} \quad (7)$$

Rate Constants.—The pH of the reaction mixtures remained practically constant in each kinetic

run, and the optical density of the dye varied with time in a good first-order manner. Pseudo-first order rate constants were computed for each run from equation 4a. The accuracy of the rate constants was not uniform, and depended on the speed of the reaction and the magnitude of the change in optical density. Standard errors ranged from 20% to less than 2%. Kinetic data for a favorable case are shown in Table III in order to demonstrate the accurate first-order course of the reactions up to better than 95% completion.

TABLE III

KINETIC DATA AT 25° FOR THE REACTION OF 10^{-5} M CRYSTAL VIOLET IN THE PRESENCE OF 0.01 M SODIUM LAURYL SULFATE AT 0.186 N SODIUM HYDROXIDE

t, min.	O.D.	10^4k, sec.$^{-1}$	t, min.	O.D.	10^4k, sec.$^{-1}$
0	0.734	..	41	0.293	5.1
4	.652	(5.9)	51	.244	5.1
7	.618	5.0	60	.211	5.2
10	.577	4.9	68	.189	5.2
13	.537	4.9	85	.160	5.1
17	.489	4.9	124	.129	5.1
25	.408	5.0	266	.124	(2.7)
35	.327	5.1	∞	.115	..

As indicated in equation 5, k is the sum of the pseudo-first order rate constants for the forward and reverse reactions. In the presence of NaLS, it was possible to measure $k^\ominus$ by approaching the equilibrium from both directions. As shown in Table IV the observed values of $k^\ominus$ were equal, proving that the final state is indeed one in which R^+ and ROH are in reversible equilibrium. As a consequence, some of the values of $k^\ominus$ listed in Table VI were obtained by approaching the equilibrium from an initial solution containing ROH rather than R^+.

TABLE IV

VALUES OF $k^\ominus$ WHEN EQUILIBRIUM IS APPROACHED FROM BOTH DIRECTIONS (0.01 M SODIUM LAURYL SULFATE, 10^{-5} M DYE, 25°)

		$10^4k^\ominus$ (sec.$^{-1}$) when equilibrium is approached from	
Dye	[OH$^-$]	R^+	ROH
Crystal violet[a]	0.0932	2.0	2.1
Malachite green	1.55×10^{-4}	1.8	1.7
Rosaniline	0.0194	0.72	0.74

[a] Dye concn., 1×10^{-6} M.

In several cases, the concentration of dye or of boric acid–sodium borate buffer was varied by factors of 4 or more. The effects were relatively small, amounting to 30% or less, as shown in Table V and by some of the data in Table VI.

TABLE V

EFFECT OF CHANGING THE BUFFER CONCENTRATION ON THE PSEUDO-FIRST ORDER RATE CONSTANT FOR THE FADING OF MALACHITE GREEN, 25°

Boric acid plus sodium borate	10^4k_f, sec.$^{-1}$	$10^4k_f^\ominus$, sec.$^{-1}$	$10^4k_f^\ominus$, sec.$^{-1}$
0.05 M	6.54	30.9	1.4
0.01 M	6.25	26.0	1.1[a]
pH in soln.	10.31	10.01	10.06

[a] Based on measurement of initial rates.

TABLE VI

SUMMARY OF PSEUDO-FIRST ORDER RATE CONSTANTS FOR THE FADING OF TRIPHENYLMETHANE DYES[a] AT 25°

Buffer	Other solutes, M	10^3[OH$^-$], M	10^4k, sec.$^{-1}$[f]	10^4k_1, sec.$^{-1}$[g]
	Crystal violet			
Boric acid–sodium	....	0.155	1.0	0.9
borate, 0.05 M	CTABr, 0.01	.0263	2.07	2.07
	CTABr, .01	.155	13	13
	CTABr, .01	.172	13.8	13.8
	NaLS, 0.01	.0288[b]	86	0.062
	NaLS, .01	.182[b]	11.2	.051
	NaLS, .01	1.15	1.99	.056
	NaLS, .01	2.97	1.42	.099
Sodium hydroxide	....	10.0	17.1	17.1
	NaCl, 0.01	10.0	16.4	16.4
	CTABr, 0.01	10.0	240	240
	NaLS, 0.01	19.8	2.0	0.21
	NaLS, .01	93.2[c]	2.0	1.2
	NaLS, .01	186	5.1	4.2
	Malachite green			
Boric acid–sodium	....	0.186	6.30	6.30
borate, 0.05 M	CTABr, 0.01	.0234	9.4	9.4
	CTABr, .01	.151	44.3	44.3
	NaLS, 0.01	.0288	4.9	1.4
	NaLS, .01	.160	1.78	1.27
	NaLS, .01	.182	2.2	1.6
Sodium hydroxide	....	10.0	140	140
	CTABr, 0.01	10.0	>300[d]	>300[d]
	NaLS, 0.01	10.0	1.1	1.1
	Rosaniline			
Boric acid–sodium	....	0.141[e]	8.1	8.1
borate, 0.05 M	....	.160	11	11
	CTABr, 0.01	.0276	6.07	6.07
	CTABr, .01	.141[e]	11	11
	CTABr, .01	.174	13.1	13.1
	NaLS, 0.01	.0287	30.8	0.195
	NaLS, .01	.191	4.02	.163
	NaLS, .01	.822	1.26	.194
	NaLS, .01	2.24	0.85	.282
Sodium hydroxide	....	10.0	130	130
	CTABr, 0.01	10.0	160	160
	NaLS, 0.01	19.4	0.73	0.38

[a] Unless indicated otherwise, the dye concentrations are 1×10^{-5} M. [b] Dye concentration 5×10^{-7} M. [c] Dye concentration 1×10^{-6} M. [d] Too fast to measure. [e] Dye concentration 2.6×10^{-6} M. [f] Or $k^\ominus$, or $k^\oplus$. [g] Or $k_f^\ominus$, or $k_f^\oplus$.

The rate constants obtained in this work are summarized in Table VI. Since $k = k_f + k_r$ and K[OH$^-$] $= k_f/k_r$, individual values of k_f and k_r could be derived. The former are included in the table. The required values of K and $K^\ominus$ were taken from Table I. Values of $K^\oplus$ were not available, but the conversion of R^+ to ROH went virtually to completion in the presence of 0.01 M CTABr, so that k_f^+ is equal to $k^\ominus$.

Table VI also lists a rate constant for crystal violet in a solution containing 0.01 M added sodium chloride. Judging by this datum, the "normal" ionic strength effect is a slight decrease in k_f. The magnitude of the observed effect is consistent with estimates made in a preceding section.

Locus of Reactions in the Presence of Sodium Lauryl Sulfate.—In the presence of CTABr, where the rate is greatly accelerated, a major fraction of the reactions must be taking place in or on the micelles. However, in the presence of NaLS, where the rate is greatly retarded, the portion of R^+ which exists in or on the micelles might conceivably be unreactive, and the decrease in rate due to the decrease in the concentration of R^+

in the bulk phase. We now wish to show that such an explanation is untenable.

First, it is evident from the data in Tables I and II that in the presence of 0.01 M NaLS, less than 0.1% of R^+ exists in the bulk phase; yet $k_f^\ominus/k_f$ at comparable pH values is always greater than 0.001, and usually greater than 0.01. Thus the decrease in rate, striking though it may be, is not nearly as great as the decrease in the amount of R^+ in the bulk phase. Furthermore, when values are calculated for the rate constants of the reverse reaction, it turns out that $k_r^\ominus$ consistently exceeds k_r for the same buffer by at least one order of magnitude. Since a major fraction of the reverse reaction is therefore taking place in or on the micelles, it follows from the principle of microscopic reversibility[7] that an equally major fraction of the forward reaction must also occur in or on the micelles.

Kinetic Analysis.—The data obtained in the *absence* of micelle-forming salts were fitted to the equation

$$k_f = k_1 + k_2[OH^-] \qquad (8)$$

which is consistent with the data of Goldacre and Phillips[2] in this pH range. Our own data, shown in Table V, indicate that catalysis by solutes other than $[OH^-]$ is unimportant in our buffers. The values of k_1 and k_2 are listed in Table VII.

TABLE VII

RATE CONSTANTS FOR THE FADING OF TRIPHENYLMETHANE DYES AT 25°

Compound	$10^4 k_1$	$10^4 k_1^{\oplus a}$	$10^4 k_1^{\ominus a}$	$10^4 k_2$	$10^4 k_2^{\oplus a}$	$10^4 k_2^{\ominus a}$
Crystal violet	0.65	<0.3	0.05₆	0.16₅	8.0	<0.0024[b]
Malachite green	3.8	3.0	1.4	1.36	27.4	≈0[b]
Rosaniline	9	4.8	0.18	1.21	4.8	<0.0066[b]

[a] Based on data obtained in the presence of 0.05 M boric acid–sodium borate buffer and 0.01 M detergent salt. [b] Upper limits for $k_2^\ominus$ based on the data obtained in the presence of NaOH are: crystal violet, <0.0023; malachite green, <0.011; rosaniline, <0.0038.

Our experience with equilibrium constants, $K^\ominus$, suggests that kinetic data obtained in the presence of micelle-forming salts in the boric acid–sodium borate buffer may quite possibly follow classical kinetic patterns, but that these data may not be comparable with the data obtained in the presence of NaOH. As a matter of fact, the values of $k_f^\oplus$ and $k_f^\ominus$ obtained in the borate buffers can plausibly be analyzed in terms of the classical scheme shown in equation 8. For example, in the presence of NaLS, $k_f^\ominus$ varies by no more than 20% in the pH range 9.5–11.0, in spite of the thirtyfold variation of $[OH^-]$. It seems reasonable to assume that the reaction is predominantly first-order in this range. The slight increase in $k_f^\ominus$ observed at pH 11.4 for crystal violet and rosaniline may possibly be due to the incursion of a second-order reaction with hydroxide ion.

The data obtained in the presence of CTABr can be analyzed similarly in terms of equation 8. Values of $k_f^\oplus$ were plotted *vs.* $[OH^-]$. The slopes are equal to $k_2^\oplus$ and the intercepts to $k_1^\oplus$. For crystal violet, the reaction is predominantly second

(7) R. C. Tolman, "The Principles of Statistical Mechanics," Oxford University Press, London, 1938.

order over the entire range, but for malachite green and rosaniline the reaction appears to be of mixed order.

The rate constants obtained in this way are listed in Table VII. It is evident that the addition of either of the two detergents results in a decrease of the first-order rate constant. On the other hand, the addition of the cationic detergent greatly accelerates the second-order reaction with hydroxide ion, whereas the addition of the anionic detergent greatly retards it.

The kinetic data obtained in the presence of NaOH do not fit quantitatively into the pattern established for the boric acid–sodium borate buffers, being consistent in this respect with the equilibrium constants. Judging by the more extensive data obtained for crystal violet (Table VI), the rate constants may not conform to simple kinetic laws. However, since the hydroxide concentration is higher in these experiments than in those involving the borate buffers, the data give additional evidence concerning the significance of the previous estimates of $k_2^\ominus$. It appears that in the presence of NaLS the evidence for a second-order reaction with hydroxide ion is probably significant for crystal violet and rosaniline, but for malachite green $k_f^\ominus$ at 0.01 M NaOH is actually somewhat smaller than at pH 10. In any case, the data confirm that $k_2^\ominus$ is very much smaller than k_2, the upper limit to $k_2^\ominus/k_2$ being about 10^{-2}.

Discussion.—From the present data, one can get only a preliminary, incomplete picture of the reaction mechanism. The key facts are: (a) The first-order reaction proceeds somewhat more slowly in the micelle phase than in the bulk phase, regardless of the charge type of the detergent. (b) For the second-order reaction, the cationic detergent causes a considerable increase in the rate constant (from four- to fifty-fold), and the anionic detergent causes a considerable decrease (to less than 1% of the value in the bulk phase). (c) Both reactions proceed more quickly in a cationic micelle phase than in an anionic one. However, there are quantitative differences: $k_1^\oplus/k_1^\ominus$ is between 2 and 25, but $k_2^\oplus/k_2^\ominus$ is greater than 700.

It is convenient to represent the effect of the micelles on the free energy of activation as the sum of two terms: (1) Owing to the micellar charge, there is a difference between the electrical potential of the bulk phase and of the reaction site when the latter is near the surface of, on the surface, or within the micelles. Thus there is a term equal to the electrical work which is involved in the transfer of an attacking ion or of an oriented dipole from the potential of the bulk phase to that of the reaction site. (2) Owing to the change in the molecular environment of the reaction site, there is a "medium effect" on the reaction. This may range all the way from a relatively trivial change in the rate constant to a major change in reaction mechanism.

In the present case, one would expect that the term due to the electrical work is very important for the second-order process in which the attacking reagent is hydroxide ion, but that it is less im-

portant or unimportant for the first-order process. This is in agreement with observation, since the second-order reaction is greatly facilitated by cationic micelles and retarded by anionic ones, whereas the first-order reaction is retarded by micelles of either charge type, although less so by cationic ones than by anionic ones.

It is possible to explain the reaction rates observed for the first-order process also by an electrostatic model, on the basis of the following plausible assumptions: The charge of R^+ is less diffuse in the transition state than in the ground state; the effective reaction medium is less polar in the micelle phase than in the bulk phase; and the reaction involves attack by a water molecule from the bulk phase, with the negative end of the dipole oriented toward the micelles. The first two assumptions lead to a medium effect so that the rate constant is smaller in the micelle phase than in the bulk phase; and the third assumption results in $k_1^\ominus/k_1^\ominus$ being greater than unity.

However, a purely electrostatic explanation can hardly be regarded as complete. In previous studies of reactions occurring at an interphase, it was necessary to consider also the accessibility and precise orientation of the reactive functional group.[8] For reactions occurring in a micelle phase, accessibility and orientation of the reactant(s) and transition state complex must similarly be important. But, at least in principle, it is more difficult to find out about these things for reactions occurring in micelles because the micelles have three-dimensional as well as two-dimensional aspects. The actual reaction site need not be at the interphase but may be located within the micelles.

One may hope to obtain further information about the reactions from the solubility ratios for the transition state complexes. In the presence of sodium lauryl sulfate, this ratio can be evaluated from our data by means of equations 9, and the results are listed in Table II. It is seen that, for

$$\frac{k_1\ominus}{k_1} = \frac{(S_1\ominus/S_1)^{\pm}}{(S_{R^+}\ominus/S_{R^+})} \qquad \frac{k_2\ominus}{k_2} = \frac{(S_2\ominus/S_2)^{\pm}}{(S_{R^+}\ominus/S_{R^+})} \qquad (9)$$

the first-order transition state, the ratio resembles that for R^+, and that for the second-order transition state, it more nearly resembles that for ROH. If, as is probable, the two transition states differ primarily in their charge type, being formulated by $[R\cdots OH_2]^{\oplus}$ and $[R\cdots OH]$, then the quotient of their solubility ratios must be ascribed to the electrostatic attraction between $[R\cdot\cdot OH_2]^{\oplus}$ and the negative charge of the host micelle. Using the data in Table II, the factor contributing to the solubility ratio of $[R\cdots OH_2]^{\oplus}$ due to electrostatic interactions with the anion micelles is thus estimated as 100 to 1000.

Application to Organic Synthesis.—The use of detergents is likely to be a powerful tool for controlling the course of ionic organic reactions. In our work, we employ an organic substrate (R^+) which exists partly or largely in the micelle phase, and which is capable of reacting either with an anion (OH^-) or with a neutral molecule (HOH).

We find that an anionic detergent (where the micelles repel the approach of an anion from the bulk phase) practically suppresses the reaction with hydroxide ion, whereas a cationic detergent (where the micelles attract the attacking hydroxide ion) accelerates this reaction so effectively that it becomes the major one.

The technique of using water and a detergent of suitable charge type as the reaction medium for ionic organic reactions has many advantages. A water–detergent medium is less expensive than certain organic media which are good solvents for electrolytes—for example, dimethyl sulfoxide or dimethylformamide—and there may be fewer undesirable side-reactions. Owing to the possibility of changing the nature or the concentration of the detergent, there are two additional variables which can be used to control the rate of the reaction or the final state of equilibrium.

Experimental Part

Materials.—The triphenylmethane dyes and detergents were the same as reported in the preceding paper. The carbinols were prepared with the assistance of P. J. Karabatsos, as follows.

The carbinol of crystal violet was prepared according to Guyot[9] by adding sodium hydroxide to a warm aqueous solution of crystal violet. The gray flaky precipitate was filtered, dried, dissolved in benzene and treated with charcoal. Addition of n-pentane to the benzene solution gave crystalline carbinol which was recrystallized another time from benzene–n-pentane. These crystals did not have a sharp melting point but decomposed at 180–200°. Guyot[9] reports a melting point of 219°.

The carbinol of malachite green was prepared according to Heertjes.[10] It was difficult to isolate pure carbinol from the precipitate which was obtained after adding sodium hydroxide to a solution of malachite green. It was probably oxidation by air which caused the formation of a tar-like impurity. The filtered, dried carbinol was dissolved in a mixture of ether and petroleum ether and treated with charcoal. This treatment did not remove the brown color of the solution. The crystalline carbinol was obtained by adding n-pentane to the solution and recrystallizing from benzene–n-pentane (m.p. 116–118°).

Solutions and Measurements.—The preparation of solutions and the measurement of rate and equilibrium constants followed techniques described previously.[3] For each of the reaction mixtures which contained boric acid–sodium borate buffer, the pH was measured at the beginning and at the conclusion of each experiment with a Beckman model GS pH meter. The drift in pH during the experiments was found to be less than 0.05 unit even for the weakly buffered solutions, and an average value was used in the calculations. All experiments were done in an air-conditioned laboratory at 25 ± 1°.

Solubility of Carbinols.—These experiments were done with the assistance of P. J. Karabatsos. In each experiment, a few milligrams of carbinol was added to a few milliliters of the appropriate medium and shaken mechanically in a volumetric flask or a sealed ampoule for periods ranging from a few hours to five days. After shaking, the solid was allowed to settle and a portion of the supernatant liquid was withdrawn, filtered, and analyzed spectrophotometrically. We did not succeed in doing the experiments in such a way that a precisely reproducible equilibrium optical density was obtained consistently.

Although the *absolute* values of the solubility were in doubt by perhaps a factor of two, the *relative* values, $S_{ROH}\ominus/S_{ROH}$, could be measured with better precision by the following technique. At pH 10.2, in the presence of 0.01 M NaLS, the carbinol is in equilibrium with a considerable amount of carbonium ion and the saturated solutions are intensely colored. In the absence of NaLS, the saturated solutions obtained at pH 10.2 were virtually colorless.

(8) (a) J. T. Davies in "Advances in Catalysis," Vol. VI, Academic Press, Inc., New York, N. Y., 1954, pp. 1–65; (b) E. Rideal, *Proc. Roy. Soc. (London)*, **A209**, 431 (1951).

(9) M. Guyot, *Bull. soc. chim.*, **1**, 937 (1907).

(10) P. M. Heertjes, *Rec. trav. chim.*, **62**, 737 (1943).

After careful filtration, the saturated solutions *containing* NaLS were diluted with the original solvent (0.01 M NaLS, pH 10.2) until the optical density at the maximum of the visible absorption band was accurately measurable. In equation 10, this optical density will be denoted by OD', and the dilution factor by f. To the filtered saturated solutions *not* containing NaLS, enough solid NaLS was added to produce a medium 0.01 M in detergent, in which a measurable fraction of the carbinol was converted to the dye. The optical density, OD'', was measured at the maximum of the visible absorption band of R⁺ after equilibrium between ROH and R⁺ had been established. The solubility ratio, $S_{ROH}\ominus/S_{ROH}$, may then be computed from equation 10.

$$\frac{S_{ROH}\ominus}{S_{ROH}} = \frac{(OD')/f}{(OD'')} \times \frac{K\ominus[OH^-]}{1 - K\ominus[OH^-]} \quad (10)$$

Values of $K\ominus$ were taken from Table I. The final results reported in Table II are average values based on 11 experiments. The accuracy is believed to be within a factor of two.

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TALLAHASSEE, FLA.

A Study of the Mechanism of Cumene Autoxidation. Mechanism of the Interaction of *t*-Peroxy Radicals[1]
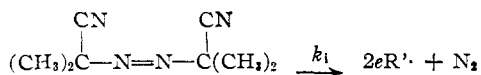
BY HARRY S. BLANCHARD

The liquid phase autoxidation of cumene has been investigated at 60° in the presence of α,α'-azodiisobutyronitrile. The rates of oxidation and yields of hydroperoxide were determined as functions of the kinetic chain lengths. Moreover, acetophenone was identified as a primary oxidation product and its yield was also determined as a function of the kinetic chain lengths. The results of the study support the idea that cumylperoxy radicals undergo a *non-terminating* interaction resulting in acetophenone and methyl radicals. The major termination product of cumene autoxidation is di-α-cumyl peroxide. The formation of acetophenone as well as the formation of di-α-cumyl peroxide support the idea that cumyloxy radicals result from the non-terminating interaction of cumylperoxy radicals. However, the fact that little α,α-dimethylbenzyl alcohol is formed indicates that if cumyloxy radicals are present, they behave differently from cumyloxy radicals resulting from the decomposition of di-α-cumyl peroxide at higher temperatures. Alternatively, both the terminating interaction resulting in di-α-cumyl peroxide as well as the non-terminating interaction resulting in acetophenone may come about *via* a common intermediate or transition state involving cumylperoxy radicals directly.

The mechanism of autoxidation of hydrocarbons has received considerable attention in recent years[2]; yet, certain aspects are still incompletely understood. In general, much of the work has been devoted to kinetic investigations, resulting in an understanding of the kinetically important propagation reaction but leading to little understanding of some other aspects of the mechanism. In particular, such kinetic studies yield little information regarding the termination reaction of autoxidation. The purpose of this paper is to present results which have a bearing on the interaction of cumylperoxy radicals. From these results, along with the over-all kinetics of autoxidation, it is now possible to write a fairly complete mechanism for the autoxidation of cumene.
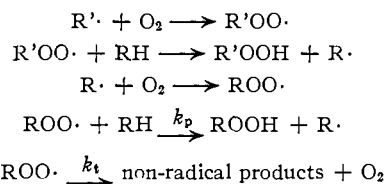
Results

Autoxidations of cumene were performed in the liquid phase at 60° in the presence of α,α'-azodiisobutyronitrile (AIBN). Under the conditions of the experiments the rates of oxygen absorption were independent of the oxygen pressure (200–760 mm.) thus indicating that only oxygenated radicals were involved in the termination reaction.[2]

The mechanism of autoxidation is now generally formulated as

$$\text{(CH}_3)_2\overset{\overset{\displaystyle CN}{|}}{C}\text{—N}=\text{N—}\overset{\overset{\displaystyle CN}{|}}{C}\text{(CH}_3)_2 \xrightarrow{k_i} 2e\text{R'} \cdot + \text{N}_2$$

$$\text{R'} \cdot + \text{O}_2 \longrightarrow \text{R'OO} \cdot$$

$$\text{R'OO} \cdot + \text{RH} \longrightarrow \text{R'OOH} + \text{R} \cdot$$

$$\text{R} \cdot + \text{O}_2 \longrightarrow \text{ROO} \cdot$$

$$\text{ROO} \cdot + \text{RH} \xrightarrow{k_p} \text{ROOH} + \text{R} \cdot$$

$$2\,\text{ROO} \cdot \xrightarrow{k_t} \text{non-radical products} + \text{O}_2$$

Application of the usual steady-state treatment to this scheme results in the expression

$$-d[\text{O}_2]/dt = k_p[\text{RH}](R_i)^{1/2}/(2k_t)^{1/2} + R_i/2 \quad (1)$$

in which R_i, the rate of initiation, $= 2ek_i[\text{AIBN}]$. In the present work, R_i has been calculated to be 1.32×10^{-6} mole l.$^{-1}$ sec.$^{-1}$ for 0.097 M AIBN based on a value of 1.15×10^{-5} sec.$^{-1}$ for k_i at 60° and a value of 0.60 for e. The value for k_i was selected from a compilation of various literature values[3] while the value of e appears established by the work of Hammond, Sen and Boozer.[4] The constancy of the data in column 4 of Table I show that (1) is obeyed rigorously in the autoxidation of cumene in chlorobenzene solution as well as in pure cumene itself.

Such a kinetic treatment provides assurance that the broad general features of the above mechanism are correct for cumene autoxidation. However, this treatment gives no insight into the termination reaction other than the fact that termination takes place in a bimolecular process involving two oxygenated radicals. Such insight can be gained from a more detailed study of the products of the reaction.

(1) Presented before the Division of Organic Chemistry at the 132nd Meeting of the American Chemical Society, New York, N. Y., September, 1957.

(2) J. L. Bolland, *Quart. Revs.*, **3**, 1 (1949); L. Bateman, *ibid.*, **8**, 147 (1954).

(3) See footnote 3 in ref. 9 for the data used.

(4) G. S. Hammond, J. N. Sen and C. E. Boozer, THIS JOURNAL, **77**, 3244 (1955).