[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NEBRASKA AND THE MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Decarboxylation of *l*-2-Methyl-2-benzenesulfonylbutyric Acid[1]

BY JAY E. TAYLOR AND FRANK H. VERHOEK

RECEIVED FEBRUARY 24, 1959

2-Methyl-2-benzenesulfonylbutyric acid has been prepared and partially resolved. Decarboxylation of the *l*-acid in the melt proceeds smoothly in the presence of catalytic amounts of base and produces optically active 2-benzenesulfonylbutane. The results are interpreted in terms of a bimolecular mechanism involving attack of the acid on the acid anion.

The rates of decarboxylation of many organic acids, such as trichloroacetic acid[2] and trinitrobenzoic acid[3] and their salts, in solution have been shown to depend upon the concentrations of the anions of the acids. It has usually been supposed that the mechanism of these reactions involves a unimolecular decomposition of the acid anion to a carbanion and carbon dioxide as the rate-determining step, followed by the rapid acquisition of a proton from some proton donor present, according to equations 1. The evidence[4] for this

$$\begin{aligned} R{-}CO_2^- &\longrightarrow R^- + CO_2 \\ R^- + HM &\longrightarrow RH + M^- \end{aligned} \qquad (1)$$

mechanism is of an indirect nature and is therefore not conclusive. Other unimolecular processes involving carbonium ions or free radicals may be eliminated as unreasonable.[4] The mechanism proposed by Schenkel and Schenkel-Rudin[5] involving a bimolecular association with a proton may also be eliminated since there is no *p*H effect beyond that associated with anion formation. A bimolecular interaction between a proton donor, such as water, and the carboxylate ion can possibly explain all known observations on anionic decarboxylations. The first-order kinetics would

$$R{-}CO_2^- + HM \longrightarrow RH + CO_2 + M^- \qquad (2)$$

be due to the excess of the solvent water, and evidence cited for the ionic intermediate may be interpreted as being due to a thermally activated or stretched carbon to carboxyl bond. Again, it may be that the ionic mechanism holds for certain of the anionic decarboxylations and the bimolecular mechanism for others. It is not easy to distinguish between the mechanisms represented by 1 and 2 because of the extreme similarity of the proposals.

A method whereby the mechanisms might be distinguished would be to prepare an optically active acid and decarboxylate it. Retention of activity would strongly support the bimolecular mechanism. Loss of activity, if the loss occurs as a result of decarboxylation, would point to the independent existence of the carbanion intermediate.

Carboxylate ions have been shown to be involved in the decarboxylation of *p*-toluenesulfonylacetic acid,[6] so an asymmetric derivative of this acid, 2-methyl-2-benzenesulfonylbutyric acid, was prepared for study. Ethyl 2-benzenesulfonylbutyrate was prepared by the procedure of Ashley and Shriner[7]; this compound was then methylated and hydrolyzed to the desired acid.

The resolution of the racemic acid represented the only major synthetic barrier encountered in this work and was achieved in part using *l*-α-phenylethylamine. The procedure was both tedious and highly time consuming.

The *l*-α-phenylethylamine salt of the 2-methyl-2-benzenesulfonylbutyric acid when precipitated from dry ether solution exhibited some unusual properties. The solubility of this salt in water at room temperature was found to be very high. However, upon standing, an appreciable quantity of the salt of the unresolved acid slowly precipitated. Since the salt was both taken into and precipitated from water solution at room temperature it was concluded that the salt must exist in two forms: one, very highly soluble in water; and, the other, moderately highly soluble. The conversion from the first form to the second appears to be catalyzed by water. The more soluble form of the salt did not reform upon drying the precipitated salt. The reason for the change in solubility is not well understood. It may be that a dimerized form (resulting from the dual negative centers in the anion) was precipitated from the ether solution and that the effect of the polar water was to associate with the negative centers and destroy the dimeric form. A very low yield of the salt of the partially resolved acid was achieved by cooling the saturated water solution to about 0° for one week.

A trial decarboxylation of the inactive acid in basic aqueous solutions indicated that the substance is very stable. The free acid decomposed only at about 300° and there was appreciable formation of tarry products. No attempt was made to identify the product (presumed to be 2-benzenesulfonylbutane) which was obtained in decidedly impure form. It came as somewhat of a surprise, therefore, when the optically active acid, recovered from its amine salt, decarboxylated very smoothly in the melt at about 200° with no tar formation. The product which distilled at 280° at atmospheric pressure was, in succeeding decarboxylations, identified as 2-benzenesulfonylbutane and, of particular interest, optical activity was observed.

---

[1] Supported in part from funds granted to the Ohio State University by the Ohio State University Research Foundation for aid in fundamental research.

[2] F. H. Verhoek, THIS JOURNAL, **56**, 571 (1934); **67**, 1062 (1945); G. A. Hall, Jr., and F. H. Verhoek, *ibid.*, **69**, 613 (1947); C. N. Cochran and F. H. Verhoek, *ibid.*, **69**, 2987 (1947).

[3] F. H. Verhoek, *ibid.*, **61**, 186 (1939); D. Trivich and F. H. Verhoek, *ibid.*, **65**, 1919 (1943).

[4] See the discussion in B. R. Brown, *Quart. Revs.*, **5**, 131 (1951).

[5] H. Schenkel and M. Schenkel-Rudin, *Helv. Chim. Acta*, **31**, 514 (1948)

[6] D. J. O'Connor and F. H. Verhoek, THIS JOURNAL, **80**, 288 (1958).

[7] W. C. Ashley and R. L. Shriner, *ibid.*, **54**, 4410 (1932).

Upon investigation of the reason for the difference in the nature of the decarboxylations of the *dl*- and the *l*-acids, it was found that the presence of a trace of any base such as an amine, sodium hydroxide, etc., also permitted a smooth decarboxylation of the *dl*- acid at 200°. Obviously a trace of the anion is necessary, clearly making this decarboxylation of the anionic type. The *l*-acid decarboxylated smoothly only because a trace of the resolving amine had not been removed during the purification process.

In order to establish that the retention of optical activity is not due to the presence of the trace of active base, the resolved acid was purified to remove the trace of contaminant and then was decarboxylated using 10 mole % triethylamine. Again the active product was formed.

Rotations were taken in both green and yellow light. It was interesting to note that the *l*-acid exhibited greater rotation in green light whereas the *d*-sulfone showed slightly more rotation in yellow light; see Table I.

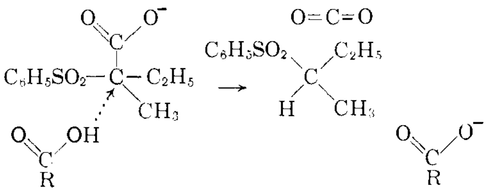
Otto[8] observed that decarboxylation of alkali metal salts of arylsulfonylacetic acids takes place in aqueous solutions at temperatures under 100°. However, the mixture of the substituted acid with its salt does not decarboxylate until a temperature of about 180° is applied to the melt, and then the reaction is quite rapid. This suggests that the activation energy is high. The presence of the methyl and ethyl groups along with the bulky benzenesulfonyl group undoubtedly provides a formidable barrier to the entering proton donor group. The lower rate and higher activation energy are thus both well explained. If the carbanion intermediate is assumed, the presence of the bulky groups should promote instability of the carbon–carbon bond and the rate of decomposition of the substituted product should be greater. This increase was not observed.

TABLE I

	C, g./100 ml.	Wave length, Å.	Temp., °C.	[α]
l-Acid[a]	10.0[c]	5893	25	−1.53°
	10.0[c]	5461	25	−2.23
	20.5[c]	5893	25	−1.82
	20.5[c]	5461	25	−2.57
d-Sulfone[b]	Pure	5893	24	+1.40
	Pure	5461	24	+1.35

[a] *l*-2-Methyl-2-benzenesulfonylbutyric acid. [b] *d*-2-Benzenesulfonylbutane. [c] The solvent was commercial absolute ethanol.

The mechanism proposed for this reaction is the bimolecular interaction



In view of the evidence presented it is difficult to present any other simple mechanism. Certainly the unimolecular carbanion proposal may be eliminated.

Whether or not a bimolecular mechanism also applies to decarboxylations in solution can only be answered by further research.

Experimental

Preparation of Sodium Benzenesulfinate.—The time-consuming and bulky procedure described[9] for the preparation of *p*-toluenesulfinic acid was very satisfactorily replaced by a method developed from early observations by Blomstrand.[10]

Two moles (252 g.) of sodium sulfite was added to 900 ml. of boiling water and immediately treated with one mole (176.6 g.) of benzenesulfonyl chloride. Then without further heating 1.8 moles (72 g.) of sodium hydroxide in 80 ml. of water was added over a period of 0.5 hour or as rapidly as possible to avoid excessive reflux. After cooling, 250 ml. of concentrated hydrochloric acid was added to precipitate the benzenesulfinic acid. The filtered precipitate was treated with about 54 g. of Na_2CO_3 and the resulting salt was recrystallized from hot water to yield 145 g. (88.5% yield) of sodium benzenesulfinate. A small additional amount of the acid was recovered by treating the filtrate with hydrochloric acid.

Preparation of Ethyl Benzenesulfonylacetate and Ethyl 2-Benzenesulfonylbutyrate.—With minor changes in detail the procedure of Ashley and Shriner,[7] starting with ethyl chloroacetate and sodium benzenesulfinate, was followed. The products were purified by recrystallization from ether at 0°.

Preparation of Ethyl 2-Methyl-2-benzenesulfonylbutyrate.—Absolute alcohol (1.4 l., prepared by adding 100 ml. of benzene to 1550 ml. of commercial absolute alcohol and distilling 250 ml. through a Vigreux column) was treated with 33.3 g. (1.45 moles) of sodium followed by 364.5 g. (1.424 moles) of ethyl 2-benzenesulfonylbutyrate. A thick curdy mixture resulted. Over a period of about 0.75 hour, 213 g. (1.5 moles) of methyl iodide was added and a clear neutral solution resulted. The alcohol was distilled off until the sodium iodide began to precipitate, and the remaining mixture was cooled and poured into about three liters of ice-water. The aqueous layer was extracted twice with ether and the ether solution was mixed with the main product, which was washed with water and dried over anhydrous calcium chloride. Decolorizing charcoal was added and the solution was filtered, leaving a total volume of about 1 liter or less. The dry ether solution was cooled to −40° or lower in order to effect crystallization. A total of five crystallizations from dry ether was necessary to achieve a reasonable purity. During the first four crystallizations, the product crystallized slowly without stirring. A solid mass from which the mother liquor was decanted formed at the bottom of the flask. In the final crystallization the ether solution was stirred as it was being cooled, giving a moderately fine-grained but filterable precipitate; 290 g. (75.5% yield) of the five times recrystallized product having a melting point of 52–53° was obtained; 61 g. (14.7%) of less pure material was recovered from the mother liquors.

Anal. Calcd. for $C_{13}H_{18}O_4S$: C, 57.75; H, 6.71. Found: C, 57.77; H, 6.84.

Preparation of *dl*-2-Methyl-2-benzenesulfonylbutyric Acid.—Five-hundredths mole (13.5 g.) of the above ester was mixed with 4.0 g. (0.06 mole) of 85% potassium hydroxide in 16 ml. of methyl alcohol. The mixture was either heated to boiling or allowed to stand for 24 hours or longer without warming in order to effect a reasonably complete reaction. The methyl alcohol solution was diluted with water and extracted with ether to remove the bulk of the alcohol. Acidification of the remaining solution yielded an oil which dissolved in ether. The water solution was extracted with ether and the combined ether solutions were dried over calcium chloride and the solvent evaporated. The resulting oil slowly crystallized upon standing. The melting point of the first material obtained was 113–118° with previous softening. A sample purified by dissolving in ethanol, allowing the solution to evaporate to crystal formation and washing with alcohol, melted, after drying, at 116.5–118°. The infrared spectrum in chloroform solution indicated strong absorption at 1720 (carboxyl), 1308 and

---

(8) R. Otto, *Ber.*, **18**, 154 (1885).

(9) F. C. Whitmore and F. H. Hamilton, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 492.

(10) C. W. Blomstrand, *Ber.*, **3**, 965 (1870).

1150 (sulfonyl) and 1080 cm.$^{-1}$; medium absorption at 2950 and 1454 cm.$^{-1}$; and weak absorption at 1605, 1588, 1040 and 1002 cm.$^{-1}$.

Anal. Calcd. for $C_{11}H_{14}O_4S$: C, 54.53; H, 5.82; neut. equiv., 242. Found: C, 54.65; H, 5.72; neut. equiv., 244.

Resolution of *dl*-2-Methyl-2-benzenesulfonylbutyric Acid.—Attempts to resolve the acid using brucine, quinine, strychnine, morphine or the *d*-base from Chloromycetin were unsuccessful. A partial resolution was achieved using *l*-α-phenylethylamine. *l*-α-Phenylethylamine *l*-malate (91.6 g., 0.349 mole) was treated with 28.6 g. (0.72 mole) of sodium hydroxide plus sufficient water to make the mixture convenient to handle. The amine was extracted with ether, the ether solution was dried over potassium hydroxide and then was combined with 84.5 g. of *dl*-2-methyl-2-benzenesulfonylbutyric acid in dry ether solution. Upon mixing the acid and the base, the salt very slowly precipitated. The mixture was allowed to stand overnight to complete the precipitation. An aqueous solution containing 63.9 g. of salt in 28.5 ml. of water was made at room temperature, but, interestingly enough, upon standing at this same temperature this solution slowly precipitated crystals of the salt which had been dissolved in it. The acid recovered from this precipitate showed no optical activity. Precipitation was allowed to continue for several days until an equilibrium condition was achieved. The resulting saturated solution then was placed in a refrigerator and upon standing one week, fairly well formed crystals were observed in low yield. Additional salt was dissolved in the mother liquor at room temperature and the above crystallization procedure repeated. After the total amount of salt had been treated in this manner a second series of crystallizations was made starting with the once-crystallized salt. The entire procedure required several months' time. A yield of 11.4 g. of air-dried salt was obtained.

The salt was treated with 10 ml. of water and 5 ml. of concentrated hydrochloric acid. The mixture was extracted three times with ether and the ether solution was washed and then evaporated to dryness yielding an optically active product. The acid thus obtained was allowed to stand about one day and then was placed in a vacuum desiccator along with a beaker of sulfuric acid. After two days, the mixture crystallized to a soft mass which slowly hardened. The first decarboxylation was made with this acid.

Further purification was achieved by dissolving the above acid in dilute potassium carbonate solution, precipitating with excess sulfuric acid and extracting with benzene using a continuous extractor. The benzene solution, upon standing at room temperature, yielded crystals of acid which showed only slight activity as compared to the fraction in solution. Evaporation of the benzene solution gave a light yellow liquid which very slowly formed a soft solid mass. Treatment of this material with cold benzene resulted in only a partial solution. The insoluble material was set aside since its rotation was $[\alpha]^{22}_{\mathrm{D}}$ −0.1° (*c* 9.6 in ethanol). The benzene solution was passed through a column of silicic acid and the benzene evaporated. After a long period of standing the resulting oil crystallized to form a solid with a light yellow color. Treatment of an alcohol solution of this solid with Norit eliminated most of the color; see Table I for the rotations. Upon allowing the alcohol solution to evaporate, long needle-like crystals of the *dl* acid formed first. Evaporation of the residual alcohol under vacuum gave a solid of melting point 86–89°. Several melting points taken during the over-all purification process indicated that the greater the proportion of the *dl*-acid the higher the melting point. The infrared spectrum is essentially indistinguishable from that of the *dl*-acid.

d-2-Methyl-2-benzenesulfonylbutyric acid was prepared from the acid recovered from the mother liquor. An ether solution of this acid was very slowly evaporated resulting in crystallization of the *dl*-acid. The remaining material (1.2 g.), purified by treating both an alcohol solution of the acid and an aqueous solution of the sodium salt with Norit, showed optical activity; $[\alpha]^{27}_{5461}$ +0.81°. No further work was done with the *d*-acid.

Decarboxylations of *dl*-2-Methyl-2-benzenesulfonylbutyric Acid.—(a) About one gram of the acid was placed in an S-shaped test-tube and the closed end of the tube was heated in a Wood's metal-bath. At a bath temperature of about 270–280°, decarboxylation accompanied by a slow distillation into the colder part of the tube was observed. There was appreciable decomposition into a tar-like material and creeping of this product along the walls of the tube to mix with the product. An obnoxious odor, presumably due to a thiol, was observed during the distillation. Dissolution of the brown distillate in ether permitted the recovery of a light yellow viscous liquid after a period of settling and upon evaporation of the ether. No further work was done with this product.

(b) Some of the *dl*-acid was mixed with water and heated in the S-shaped test-tube as before. Again, the dark tarry products were obtained, and the temperature of decarboxylation was similar to that of the first experiment.

(c) In the next experiment, a small amount of the amine salt was mixed with the *dl*-acid and the mixture heated. In this case, the decarboxylation proceeded quite similarly to the decarboxylation of the active acids reported below. The product was water white and the reaction proceeded at a much lower temperature than was observed previously with the *dl*-acid.

(d) An experiment was done in which the *dl*-acid was mixed with a trace of sodium hydroxide and the mixture heated. Again, the reaction proceeded similarly to the decarboxylation of the active acid, with a water-white product and a smooth evolution of carbon dioxide at about 200°. There was some charring in the reaction flask, but this was probably due to decomposition of the residual sodium salt.

(e) From the experiments described above it appeared that the ideal base for decarboxylation of this acid should be both reasonably strong and volatile. Ammonia does effect the decarboxylation, but it was not used in the following experiments because of the possibility of amide formation. Triethylamine was chosen primarily because a bottle of it was close at hand at the time it was needed.

The *dl*-acid (0.500 g., 0.0021 mole) was treated with 0.028 ml. (0.0002 mole) of triethylamine and this mixture was heated at atmospheric pressure using a Wood's metal-bath. Carbon dioxide evolution began at a bath temperature of 175° and proceeded rapidly at 195°. Very little discoloration due to degradative decomposition was noted since the amine distilled out as the acid decarboxylated.

The reaction and distillation flask was an H-shaped tube made of 10-mm. tubing sealed at both of the bottom ends. The acid was placed on one side of the H-tube and a thermometer above it. The other side was connected to a vacuum source. Glass wool very adequately prevented bumping during the distillation.

The 2-benzenesulfonylbutane distilled smoothly at 211–213° at 43 mm. pressure. The product was evacuated over H_2SO_4 for 24 hours to remove any traces of amine which remained. There was no indication of the presence of any acid.

The infrared spectrum of both the pure liquid and a chloroform solution showed strong absorption at 1146 and 1305 cm.$^{-1}$ (sulfonyl group), medium absorption at 1088, 1453 and 2994 cm.$^{-1}$ and weak absorption at 932, 962, 1002, 1023, 1388 and 1588 cm.$^{-1}$. In the pure liquid, additional medium to strong absorption was observed at 690, 726, 742 and 764 cm.$^{-1}$. Support for the presence of aliphatic carbonyl, 1725–1690 cm.$^{-1}$, was lacking.

Anal. Calcd. for $C_{10}H_{14}O_2S$: C, 60.57; H, 7.12. Found: C, 60.52; H, 7.31.

Formation of *d*-2-Benzenesulfonylbutane by Decarboxylation of *l*-2-Methyl-2-benzenesulfonylbutyric Acid.—(a) Sixty-one hundredths gram of the unpurified *l*-acid was placed in an S-shaped tube. Gas evolution was observed at about 180°. The reaction mixture was then heated to 290–320°, yielding a water-white distillate (b.p. about 282°) and negligible tar. The distillate was dissolved in ether, washed with sodium bicarbonate solution and the ether was evaporated, yielding 0.46 g. of product (92% yield). A second run gave a 96% yield. The product was found to be optically active.

(b) Decarboxylation of the purified *l*-acid resulted in formation of brown, foul smelling decomposition products similar to the pure *dl*-acid. This indicated that the contaminating amine salts had been effectively removed.

(c) The pure *l*-acid (0.500 g. or 0.0021 mole) was treated with 0.028 ml. (0.0002 mole) of triethylamine and this mixture was heated in an S-shaped test-tube. The decarboxylation proceeded similarly (175–195°) to that of the *l*-acid of part a and the *dl*-acid of part e. The resulting 2-benzenesulfonylbutane, distilled under vacuum using glass wool to prevent bumping (211–213° at 43 mm.), was optically active. The product weighed 0.389 g. (95% yield); see Table I for rotations. Another preparation of the sulfone 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.

LINCOLN 8, NEB.
COLUMBUS 10, OHIO

[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]

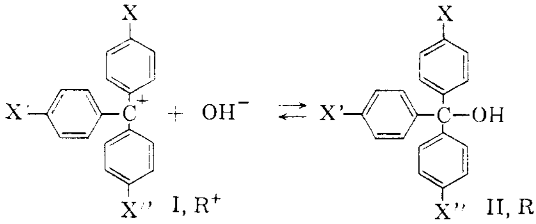
There are theoretical as well as practical reasons for the study of reactivity in the presence of micelles. On the practical side, industrial recipes for carrying out reactions often involve the solubilization of a reactant, a well-known example being emulsion polymerization.[2-4] On the theoretical 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]

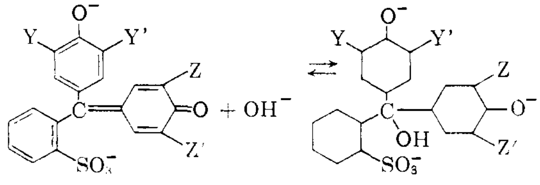
We now report kinetic and equilibrium studies in the presence of micelle-forming salts for reactions of two different charge types: the fading in alkaline solution of triphenylmethane dyes (reaction 1) and of sulfonphthalein indicators (reaction 2). Rates and equilibrium constants for reactions such 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 forward reactions (fading)

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

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



I, R^+ II, ROH (1)



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

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.

---

[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.