ably good agreement with the somewhat approximate value 2.28 reported in Table II. It would appear from this that the presence of the three fluorines, which greatly increases the acidity of the molecule, does not greatly alter the moment of the carboxyl group. In view of the evidence which has been mentioned or discussed, it appears probable that the hydroxyl hydrogen does not lie to any great extent in the plane of the rest of the carboxyl group and that the hydroxyl group is undergoing a torsional oscillation or restricted rotation with the hydrogen, on an average, well outside of this plane.

PRINCETON, NEW JERSEY RECEIVED MARCH 19, 1951

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Chemistry of Persulfate. II. The Reaction of Persulfate with Mercaptans Solubilized in Solutions of Saturated Fatty Acid Soaps[1]

BY I. M. KOLTHOFF AND I. K. MILLER[2]

Mercaptans containing 8 to 12 carbon atoms solubilized in solutions of saturated fatty acid soaps are oxidized by persulfate to disulfide. Evidence is given that the first step in the persulfate oxidation of solubilized mercaptans is a reaction of persulfate with the soap forming carboxylate free radicals which oxidize the solubilized mercaptan to mercaptyl free radicals which combine to form disulfide. In the absence of mercaptan persulfate reacts with saturated fatty acid soaps removing the carboxylate group. The disappearance of persulfate in soap solutions is first order and the reaction rate is the same in the presence as in the absence of mercaptan and is independent of the soap concentration over a wide range of concentrations. The oxidation of solubilized normal mercaptans by persulfate is zero order with regard to mercaptan concentration over a wide range of concentrations. Solubilized *n*-octyl and *n*-dodecyl mercaptans are oxidized by persulfate at the same rate.

From the viewpoint of establishing the mechanism of persulfate initiation of emulsion polymerizations, it is of interest to understand the mechanism of the reaction of persulfate with water-insoluble compounds solubilized in soap solutions, especially those compounds which are used in emulsion polymerization recipes.

The oxidation of solubilized mercaptans by persulfate was found to be a satisfactory reaction for such a study because this reaction proceeds at a readily measurable rate at 50° and the disappearance of both reactants can be easily followed. Relatively high molecular weight mercaptans (C_8 to C_{14}) were used because of the small water solubilities of these mercaptans. The results of this study also contribute to an understanding of the mechanism of the action of mercaptans as chain transfer agents in emulsion polymerizations.

Preliminary investigations on the reaction of persulfate with solubilized mercaptans were first reported by Canterino and Reynolds[3] as part of a study designed to find a simple method of characterizing mercaptans with regard to their chain transfer efficiencies in emulsion polymerizations. These workers studied the rate of persulfate oxidation of mercaptans solubilized in solutions of a commercial soap mixture composed of the sodium salts of palmitic, stearic and oleic acids. Further systematic studies in this Laboratory, showed that the reaction of persulfate with mercaptans solubilized in soaps, which are partly or entirely composed of unsaturates, is not a simple oxidation of mercaptan to disulfide but involves the addition of mercaptan to the unsaturates in the soap. The work discussed in this paper was carried out using soaps prepared from saturated fatty acids.

Experimental

Materials. *n*-Dodecyl mercaptan was a product obtained from Dr. C. S. Marvel of the University of Illinois, b.p. 114–116° (6.5 mm.), $n^{20}\text{D}$ 1.4589. The *t*-octyl and *t*-tetradecyl mercaptans were research grade products obtained from Sharples Corp. Research grade *n*-octyl mercaptan was obtained from the U. S. Rubber Co. The saturated fatty acids used were Eastman Kodak Co. products. Merck and Co., Inc., potassium persulfate was recrystallized twice from conductivity water and dried in a vacuum desiccator at room temperature. Sodium carbonate and bicarbonate used in the buffer system were reagent grade chemicals.

Analytical Methods.—Mercaptan was determined by amperometric titration with silver nitrate in ammoniacal ethanol solution according to the method of Kolthoff and Harris.[4] Interference of persulfate with the mercaptan determination was prevented in two different ways. (1) Soap solutions containing small amounts of persulfate (0.01 *M*) were added to 90% ethanol containing ferrous ion in about fivefold excess over the persulfate present. After stirring for 15 minutes an excess of ammonia was added and the titration was performed. (2) In the presence of large amounts of persulfate (0.1 *M*) it was necessary to separate the mercaptan from the aqueous persulfate solution prior to titration of the mercaptan. This was accomplished by extraction of the fatty acid and mercaptan from an acidified sample of the soap solution into benzene. The benzene solution was added to ethanol, excess ammonia added and the mercaptan titrated by the amperometric method. Disulfide was determined by reduction to mercaptan according to the method of Kolthoff, Laitinen, *et al.*,[5] followed by amperometric titration of the mercaptan. Persulfate was determined polarographically[6] after extraction of the fatty acid and mercaptan from the acidified soap solution with benzene. To determine the total organic acids present in a soap solution, 25 ml. of the solution was acidified and shaken with 25 ml. of benzene. A 25-ml. portion of distilled absolute ethanol was added to the benzene extract and enough water to cause turbidity. The turbidity was then removed by addition of a few drops of ethanol and the solution was boiled until the odor of benzene could no longer be detected in the vapor. After dilution with 50 ml. of purified ethanol the acidity of the solution was determined by titration with

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[1] This work was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the synthetic rubber program of the United States Government.

[2] From a Ph.D. thesis submitted by I. K. Miller to the Graduate School of the University of Minnesota, 1950.

[3] P. J. Canterino and W. B. Reynolds, private communication.

[4] I. M. Kolthoff and W. E. Harris, *Ind. Eng. Chem., Anal. Ed.*, **18**, 161 (1946).

[5] I. M. Kolthoff, D. R. May, P. Morgan, H. A. Laitinen and A. S. O'Brien, *ibid.*, **18**, 442 (1946).

[6] I. M. Kolthoff, L. S. Guss, D. R. May and A. I. Medalia, *J. Polymer Sci.*, **1**, 340 (1946).

aqueous sodium hydroxide solution using phenolphthalein as the indicator. Carbon dioxide in solutions of soap and persulfate was determined gravimetrically[7] after adding acid which contained ferrous sulfate to reduce the persulfate.

The solubilities of mercaptans in soap solutions were determined by measurement of the amount of mercaptan necessary to cause a permanent increase in turbidity of soap solution. In each determination a series of oxygen-free portions of the soap solution, containing varying amounts of mercaptan were rotated at 50° for 100 hours, then the turbidities of the samples were measured with a special turbidimeter thermostated at 50°. At mercaptan concentrations below the saturation value the turbidity of the solution remained essentially the same as that of the mercaptan-free soap solution but at mercaptan concentrations above the saturation value a marked turbidity was observed due to the presence of emulsified mercaptan.

Sulfate was determined by amperometric titration in 30% ethanol with lead nitrate.[8]

Experimental Method.—The experiments were carried out in a reaction vessel as shown in Fig. 1. The lauric acid and mercaptan were bubbled with oxygen-free nitrogen at 50° in a flask B while a solution containing an amount of sodium hydroxide equivalent to the lauric acid used and the buffer salts was made oxygen-free in the inlet tube A. The solutions were then mixed and stirred for 24 hours to solubilize the mercaptan, whereupon oxygen-free persulfate solution was added to the soap mercaptan mixture through A. Samples for analysis were forced out of the vessel through tube C by nitrogen pressure. Unless otherwise stated, all the solutions were buffered at a *p*H of 10 by the addition of 0.2 g. of sodium bicarbonate and 0.3 g. of anhydrous sodium carbonate per 100 g. of solution.

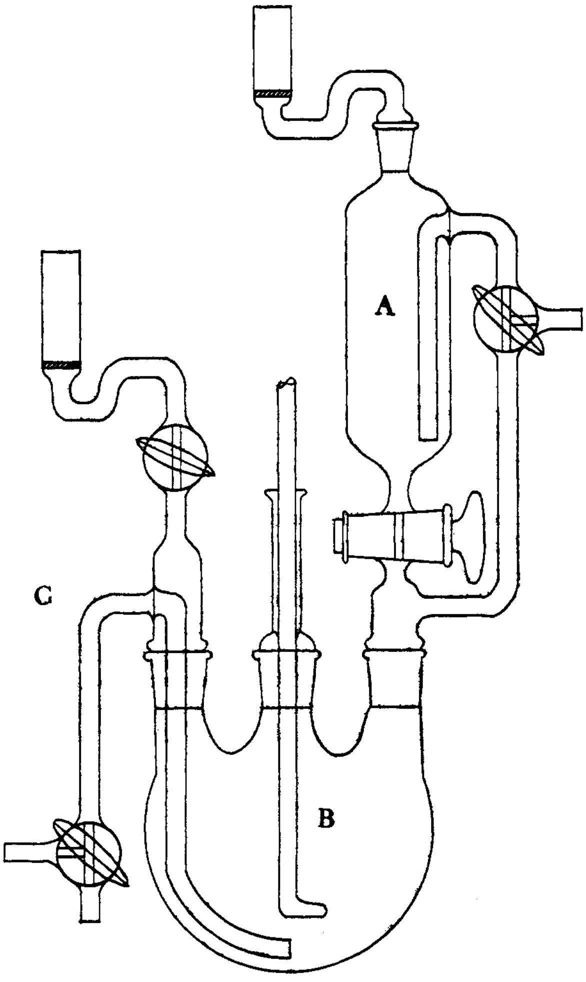

Fig. 1.—Reaction vessel.

Experimental Results

Mercaptan Solubilities.—The solubility of *n*-dodecyl mercaptan in water at 50° was found to be 3×10^{-5} *M*, in 5% sodium laurate solution 1.1×10^{-2} *M* and in 10% sodium laurate 2.6×10^{-2} *M*.

Stoichiometry and Reaction Products.—The results in Table I show that the over-all reaction between persulfate (0.01 *M*) and *n*-dodecyl mercaptan (0.02 *M*) solubilized in 10% sodium laurate solution buffered at *p*H 10 is given by the equation

$$S_2O_8^{=} + 2C_{12}H_{25}SH \longrightarrow 2HSO_4^- + C_{12}H_{25}SSC_{12}H_{25} \quad (1)$$

TABLE I

THE STOICHIOMETRY AND PRODUCTS OF THE REACTION OF POTASSIUM PERSULFATE WITH *n*-DODECYL MERCAPTAN SOLUBILIZED IN 10% SODIUM LAURATE SOLUTION AT 50° (*p*H 10)

Concentration	Mercaptan	Persulfate	Disulfide[b]	Sulfate
Initial[a]	19.50, 19.53	9.75, 9.75	.....	0.2, 0.3
Final	3.40, 3.44	1.68, 1.65	8.0, 8.0	16.1, 16.0
Change	16.10	8.09	8.0	15.8

[a] Millimoles per liter. [b] The disulfide was isolated and identified.

Kinetics.—From the results given in Figs. 2 and 3 it appears that in the absence of mercaptans

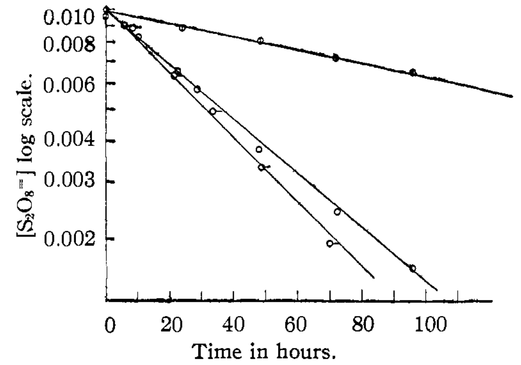

Fig. 2.—Disappearance of persulfate in oxygen-free 10% sodium laurate solution at 50°, *p*H 10.0: O, mercaptan present; O-, mercaptan absent; ⦶, aqueous solution at *p*H 10.

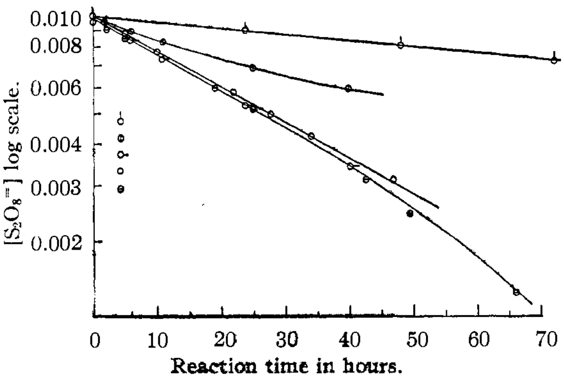

Fig. 3.—Reaction of persulfate with sodium caprate at 50°, *p*H 10.0: ⫰, buffer *p*H 10; ⦶, 0.001 *M* Na caprate; O-, 0.01 *M* Na caprate; O, 0.05 *M* Na caprate; ⊖, 0.75 *M* Na caprate.

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[7] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Company, New York, N. Y., 1943.

[8] I. M. Kolthoff and Y. D. Pan, THIS JOURNAL, **62**, 3332 (1940).

persulfate reacts with laurate and caprate and that persulfate disappearance in oxygen-free buffered solutions is a first order reaction. In a 10% laurate solution buffered at *p*H 10 the rate of disappearance of persulfate is about four times as great as in the buffer without soap (Fig. 2). The results represented in Fig. 3 show that in the buffered caprate solutions the rate of disappearance of persulfate is independent of the caprate concentration when the caprate concentration is varied between 0.01 and 0.75 *M*.

In soap solutions the rate of disappearance of persulfate was found to be the same in the presence as in the absence of mercaptan. The rate of mercaptan consumption in 10% laurate solution 0.11 *M* in persulfate was found to be independent of the initial mercaptan concentration between mercaptan concentrations of 10 millimoles per liter and the saturation value of 26 millimoles per liter (see Fig. 4). Normal octyl and normal dodecyl mercaptans disappear at the same rate in this medium but tertiary octyl and tertiary tetradecyl mercaptans are consumed about half as rapidly as the normal mercaptans as shown in Figs. 5 and 6. From Fig. 7 it is evident that the rate of consumption of *n*-dodecyl mercaptan in 10% sodium laurate solution is first order with respect to persulfate concentration and from Fig. 8 that the rate of persulfate oxidation of solubilized mercaptan is independent of the sodium laurate concentration between 7.5 and 15% sodium laurate.

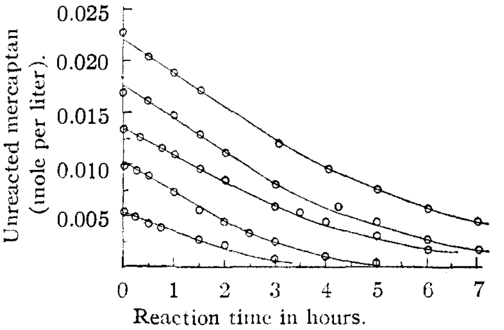


Fig. 4.—Oxidation of *n*-dodecyl mercaptan in 10% sodium laurate solution by potassium persulfate (0.11 *M*) at 50° (effect of mercaptan concentration).

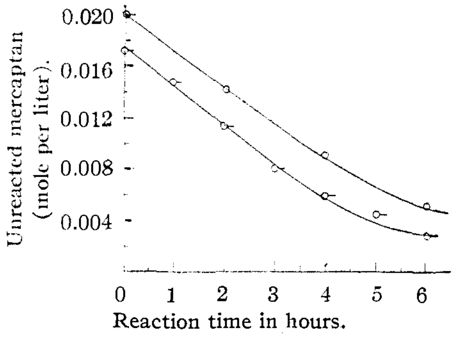


Fig. 5.—Oxidation of primary mercaptans in 10% sodium laurate solutions by 0.11 *M* potassium persulfate at 50° (oxygen absent): ○, *n*-octyl; ○-, *n*-dodecyl.

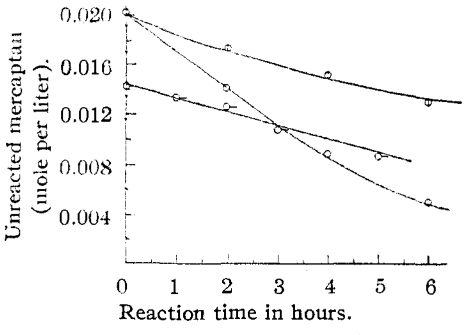


Fig. 6.—Oxidation of primary and tertiary 0.11 *M* mercaptans in 10% sodium laurate solutions by 0.11 *M* potassium persulfate at 50° (oxygen absent): ⦶, *t*-tetradecyl; ○, *n*-octyl; ○-, *t*-octyl.

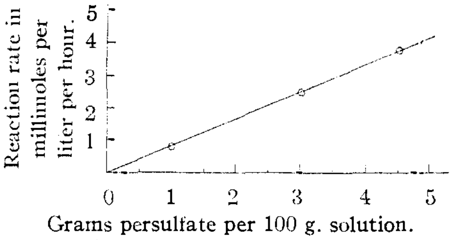


Fig. 7.—Rate of oxidation of mercaptan in 10% sodium laurate solution as a function of persulfate concentration.

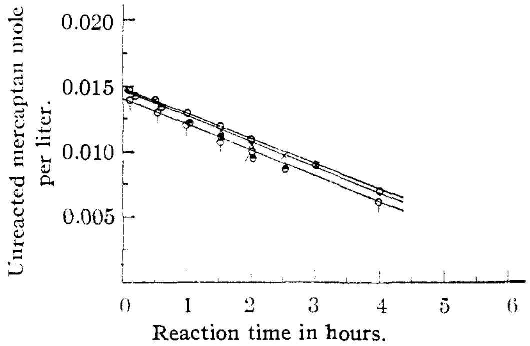


Fig. 8.—Oxidation of *n*-dodecyl mercaptan by 0.11 *M* potassium persulfate in sodium laurate solutions at 50 (effect of soap concentration): ×, 7.5% soap; ●, 10.0% soap; ○, 12.5% soap; ♀, 15.0% soap.

Figure 9 reveals that *n*-dodecyl mercaptan solubilized in sodium laurate solution is oxidized by persulfate much more rapidly at *p*H 13 than at a *p*H of 10. The rate of persulfate disappearance in sodium laurate solution in the absence of mercaptan was found to be essentially the same at *p*H 10 and 13. In all the reported experiments using normal mercaptans the oxidized mercaptan was recovered quantitatively in the form of disulfide.

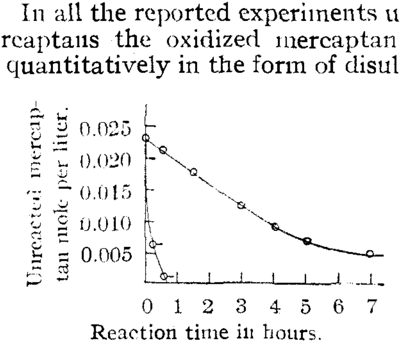


Fig. 9.—Oxidation of *n*-dodecyl mercaptan in 10% sodium laurate solution by persulfate at 50° at *p*H 10 and 13: ○, *p*H 10; ○-, *p*H 13; free of soap.

The observation that persulfate disappears more rapidly in buffered 10% sodium laurate solution than in the soap-free buffer indicates that persulfate reacts with the soap. Fichter and Suenderhauf[9] have shown that propionic and acetic acids are oxidized by persulfate in aqueous solution with removal of the carboxyl group of the acids. To determine whether persulfate reacts with the higher fatty acid soaps, the reaction of persulfate with sodium laurate and with potassium palmitate was studied. In these experiments the disappearance of both persulfate and the carboxyl group of the fatty acid were measured, also the amount of carbonate formed was determined. The reaction of persulfate with potassium palmitate was studied both in the presence and absence of *n*-hexyl mercaptan. The solutions were buffered at *p*H 10 with a carbonate-free borax buffer. The results are given in Table II.

TABLE II

THE REACTION OF PERSULFATE WITH SODIUM LAURATE AND WITH POTASSIUM PALMITATE IN THE PRESENCE AND ABSENCE OF *n*-HEXYL MERCAPTAN AT 50°

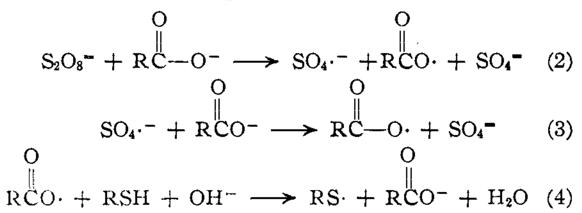
Solution	Persulfate consumed, mole/liter	Carboxyl group consumed, mole/liter	Carbonate formed, mole/liter
0.01 *M* $K_2S_2O_8$ .01 *M* Na Laurate[a]	0.00955	0.0052	0.0006
.1 *M* $K_2S_2O_8$ .1 *M* Na Laurate[a]	.0970	.0341	0.013
.104 *M* $K_2S_2O_8$ .0660 *M* K Palmitate[b]	.0255	.0084	....
.100 *M* $K_2S_2O_8$ .0683 *M* K Palmitate .0700 *M* *n*-Hexyl[b] Mercaptan	.0348	.0003	...

[a] Reaction time 144 hours. [b] Reaction time 24 hours.

Evidence was obtained that the reaction of persulfate with saturated fatty acid soaps is very complex, leading to a large number of reaction products. No attempt was made to make a complete analysis of the reaction mixture. It was established, however, that carbonate is formed, evidently by decarboxylation of the soap. In the presence of oxygen, benzene extractible compounds containing peroxidic oxygen were formed but in the absence of oxygen no peracids, hydroperoxides or peroxides soluble in benzene were formed. In the presence of solubilized mercaptan no decomposition of the soap was found.

Discussion

Reaction Mechanism.—The following mechanism is proposed for the reaction of persulfate with mercaptans solubilized in solutions of saturated fatty acid soaps.



$$S_2O_8^{=} + \mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{-O^-} \longrightarrow SO_4\cdot^- + \mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{O}\cdot + SO_4^{=} \qquad (2)$$

$$SO_4\cdot^- + \mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{O^-} \longrightarrow \mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{-O}\cdot + SO_4^{=} \qquad (3)$$

$$\mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{O}\cdot + RSH + OH^- \longrightarrow RS\cdot + \mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{O^-} + H_2O \qquad (4)$$

$$2RS\cdot \longrightarrow RSSR \qquad (5)$$

The over-all stoichiometry of reactions (2) through (5) is consistent with the observed stoichiometry given by equation (1). There are two points of evidence that the first step in the oxidation of solubilized mercaptans by persulfate at *p*H 10 is the reaction of persulfate with the soap according to reaction (2); (a) the rate of persulfate decomposition in a given sodium laurate solution is the same in the presence or absence of mercaptan, and (b) the rate of oxidation of solubilized normal mercaptans by persulfate is independent of the molecular weight of the mercaptan and of mercaptan concentration over a wide concentration range.

Further evidence in support of the proposed mechanism comes from the observation that the carboxyl group of the soap disappears when persulfate and the soap react in the absence of mercaptan but in the presence of mercaptan no disappearance of carboxyl group is observed. Decarboxylation is believed to occur in the absence of mercaptan through loss of CO_2 by the carboxylate radicals formed in reaction (2).

In order to account for the disappearance of equivalent amounts of persulfate and mercaptan observed with normal mercaptans at mercaptan concentrations above 0.008 *M*, it must be assumed that all of the carboxylate radicals formed by reactions (2) and (3) react with mercaptan according to reaction (4). With tertiary mercaptans and with normal mercaptans at very small concentrations this condition is evidently not met as evidenced by the fact that the rate of oxidation of solubilized tertiary mercaptans and normal mercaptans at low concentrations is smaller than the rate of persulfate disappearance in the soap solution. The rate of persulfate oxidation of *n*-dodecyl mercaptan solubilized in 10% sodium laurate solution was observed to be much greater at *p*H 13 than at *p*H 10. It is believed that a direct reaction of persulfate with mercaptan occurs in strongly alkaline medium. Mercaptans are very weak acids with an ionization constant of the order of 10^{-11}. At a *p*H of 10 practically all the mercaptan is present in the soap micelles. However, at a *p*H of 13 a considerable fraction of the mercaptan is present as mercaptide ions outside the micelles, where they may react directly with persulfate. This interpretation is supported by the fact that the rate of reaction of mercaptan with persulfate in aqueous solutions increases with increasing alkalinity of the solution (see Fig. 10).

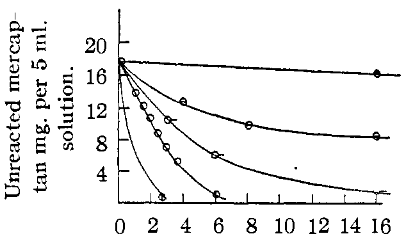


Fig. 10.—Oxidation of *n*-dodecyl mercaptan by persulfate in aqueous solution at 50° (effect of *p*H): ●, neutral; ⊖, *p*H 10; O-, *p*H 12; O, 10% sodium laurate *p*H 10; ⦶, *p*H 13.

The rate of persulfate disappearance in laurate or

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[9] F. Fichter and E. Suenderhauf, *Helv. Chim. Acta*, **16**, 338 (1933).

caprate solutions both in the presence and absence of mercaptan was found to be first order with respect to persulfate and independent of soap concentration over a wide concentration range. With the assumption that reaction (2) is rate-determining, the observed zero order dependence of the rate of persulfate oxidation of solubilized mercaptans on soap concentration (above the critical concentration) is consistent with the proposed mechanism.

Evidence that free radicals are formed by the reaction of persulfate with saturated fatty acid soaps is provided by the observation that compounds containing active oxygen (peroxides or hydroperoxides) are formed when sodium laurate, myristate or palmitate is oxidized by persulfate in the presence of oxygen. It is believed that the carboxylate free radicals formed by reactions (2) and (3) lose carbon dioxide to form alkyl radicals which react with oxygen to form peroxidic compounds.

MINNEAPOLIS, MINNESOTA RECEIVED APRIL 27, 1951

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE, AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Ionization Constants of Some *p*-Substituted *p'*-Dimethylaminoazobenzenes[1]

BY MAX T. ROGERS, TOD W. CAMPBELL AND RUSSELL W. MAATMAN

p-Dimethylaminoazobenzene and its *p'*-substituted derivatives add a proton in dilute acid and a second in strong acid solutions, and this work was undertaken to determine the acidity constants of the mono- and diprotonated bases. Values of pK_{1a} and pK_{2a} for the addition of the first and second protons to *p*-X-*p'*-dimethylaminoazobenzene where X = -H, -Cl, -I, $-CH_3$, $-C(CH_3)_3$, $-NO_2$, -SCN, -SeCN and $-OCH_3$, have been measured spectrophotometrically. The results provide additional evidence that the first proton is added to an azo nitrogen atom and the second to the dimethylamino nitrogen atom of the molecule. The effect of the *p*-substituents on the proton affinity of the nitrogen atoms is in the same order as the net electron affinities of the groups as measured by the Hammett substituent constant σ. The substituent constants for *p*-SCN and *p*-SeCN are nearly equal to that of the *p*-NO_2 group.

Introduction

The behavior of dimethylaminoazobenzene, and related compounds, in acid solutions has been studied for many years and various structures have been proposed for the ions; Hantzsch[2] showed that two series of mono-acid salts could be prepared—an unstable orange-yellow series in which the proton was probably on the amino-nitrogen, and a stable deeply-colored series in which the proton was considered to be on an azo nitrogen atom. Kehrmann[3] studied the spectra and showed that a second and a third proton could be added, each ion having a characteristic spectrum.

We have prepared a series of *p*-substituted dimethylaminoazobenzene derivatives and have measured their absorption spectra in 50% alcohol solution and in solutions of various known acidities.

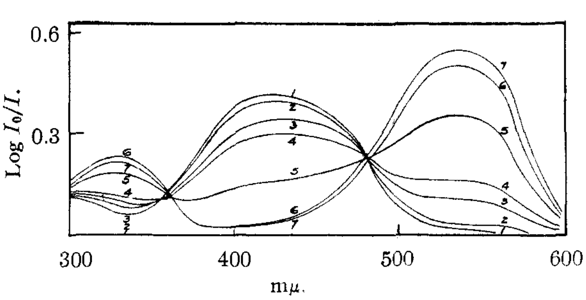
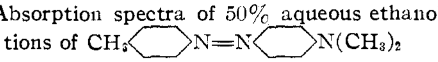


Fig. 1.—Absorption spectra of 50% aqueous ethanol solutions of 

Curve	1	2	3	4	5	6	7
*p*H	6.75	3.85	2.89	2.75	1.96	..	..
N	..	..	..	..	..	2.06	4.12

The equilibrium constants for addition of the first and second protons have been determined from the absorption spectra of the solutions and the resulting values have been correlated with the ability of the substituent groups to increase or decrease the electron density on the nitrogen atoms. The ionization exponents are approximately linear functions of Hammett's[4] substituent constants for the substituent groups and the reaction constants ρ for the first and second proton additions have been found. The behavior of the ionization constants with change of *p*-substituent is consistent with, and provides evidence for, the structures which have been assigned to the ions.

Experimental

Apparatus and Materials.—The preparation and characterization of the dyes are described elsewhere.[5] The absorption spectra were measured using a Beckman model DU spectrophotometer and 1 cm. Corex cells; spectra were recorded from 300 to 600 mμ at room temperature. A Beckman *p*H meter and glass electrode were used for *p*H measurements.

Methods.—The absorption spectra of unbuffered solutions of *p*-methyl-*p'*-dimethylaminoazobenzene in 50% aqueous ethanol of various *p*H values are shown in Fig. 1. Two isobestic points are observed and the ionization constants can be calculated without correction for a "medium effect" by the equation[6,13]

$$pK_1 = pH - \log\left(\frac{E - E_{BH^+}}{E_B - E}\right) - \log\frac{f_B}{f_{BH^+}} \quad (1)$$

where E_B, E_{BH^+} are the molar extinction coefficients of base and first ion and E is the apparent molar extinction coefficient at a given *p*H (all measured at one wave length). The ratio f_B/f_{BH^+} of the activity coefficients of base and ion is taken equal to unity since the dye concentrations are about 10^{-4} molar. Since the molar dye concentration and cell length are constant for a series of measurements optical den-

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(1) Abstracted from the Doctoral Thesis of R. Maatman, Michigan State College, 1950; presented at the 113th National Meeting of the Am. Chem. Soc., 1948.

(2) A. Hantzsch, *Ber.*, **41,** 1171 (1908); **52,** 509 (1919); **63,** 1760 (1930); etc.

(3) F. Kehrmann, *ibid.*, **48,** 1933 (1915).

(4) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Ch. VII, Ch. IX.

(5) T. W. Campbell, D. A. Young and Max T. Rogers, THIS JOURNAL, **73,** Dec. (1951).

(6) A. Thiel, *Fortschr. Chem. Physik u. physik. Chem.*, **18,** 38 (1924).