termined. The discrepancy, which exceeds the experimental error, may be significant but will require additional study before it can be explained.

Acknowledgments.—National Science Foundation support of the program of which this work was a part is gratefully acknowledged. The authors are also indebted to Mr. Richard Merrill who developed a computer program for obtaining the power series equations by least squares, to Miss Evelyn Taylor of our computing department, and to the Lynn Digital Computations Department of the General Electric Company for use of their IBM 704 computer.

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[CONTRIBUTION FROM THE SCHOOL OF MINES AND METALLURGY, UNIVERSITY OF MINNESOTA]

The Decomposition of Xanthate in Acid Solution

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RECEIVED AUGUST 12, 1957

A kinetic study of the decomposition of xanthate in acidified aqueous solutions using spectrophotometric measurements has shown that xanthate and xanthic acid are virtually in equilibrium and that the dissociation constant is 0.020 ± 0.001. The instability of xanthate solutions in the acid range is due to the monomolecular decomposition of xanthic acid with a rate constant of 4.3 ± 0.21 minute^{-1}.

The alkali metal xanthates, an important group of collectors for sulfide minerals, are known to be quite unstable in acidified aqueous solution. This presents a problem both in research and in plant operation with regard to the actual concentration of xanthate present in pulp solution.

The acid decomposition of xanthates has been studied by several investigators, all of whom assumed the reaction to be an ionic combination of xanthate and hydrogen ion to form xanthic acid with subsequent decomposition of the last-named compound into alcohol and carbon disulfide. Von Halban and his associates[1,2] studied the rate of decomposition by mixing xanthate solutions with hydrochloric acid, stopping the reaction at suitable time intervals by the addition of sodium carbonate and then analyzing the solutions by iodimetric titration. King and his associates[3–5] measured the rate from the increase in vapor pressure, primarily due to the formation of carbon disulfide. Cook and Nixon[6] attempted to follow the decomposition by measuring *p*H at different time intervals with a *p*H meter.

All of these investigators have assumed that xanthate and xanthic acid were in equilibrium. Using this assumption, they were able to calculate the dissociation constant for xanthic acid from the decomposition rate data. However, no experimental proof for this assumption has been given.

In the present paper it will be shown that the application of an ultraviolet spectrophotometer, particularly in the low *p*H range where the decomposition is extremely rapid, leads to an important implication as to the mechanism of the decomposition reaction.

Experimental

It has been reported by Hagihara[7] and by Bushell and Malnarich[8] that potassium ethyl xanthate in aqueous solution has a light absorption peak at a wave length of 301 mμ, this serving as a convenient basis for the colorimetric analysis of the substance.

The experimental procedure for the measurement of the decomposition rate consisted of mixing xanthate solutions with a known quantity of either hydrochloric or acetic acid, transferring the mixture to an absorption cell and measuring the optical density of the solution at suitable time intervals. Potassium ethyl xanthate used in this experiment was prepared in the usual manner[9] and a Beckman DU Quartz Spectrophotometer with a 1 cm. path-length quartz cuvette was used for the optical density measurements. All the experiments were made at room temperature, 23.5°.

It is possible that decomposition of xanthate may also be brought about by oxidation or by the action of alkali, and Taylor and Knoll[10] have listed the most probable reactions as

Oxidation:

$$4X^- + 2H_2O + O_2 \longrightarrow 2X_2 + 4OH^-$$

Action of alkali:

$$NaX + NaOH \longrightarrow CSONaSNa + C_2H_5OH$$

$$NaX + 2NaOH \longrightarrow CS(ONa)_2 + NaSH + C_2H_5OH$$

$$NaX + NaSH \longrightarrow CS(SNa)_2 + C_2H_5OH$$

Prior to the study of the decomposition of xanthate by acid, the extent of the effects of oxidation and of the addition of alkali were examined briefly.

Effect of Oxygen.—The decomposition of xanthate with atmospheric oxygen was tested by simultaneously agitating and aerating 2500 ml. of 7.5×10^{-5} mole per liter (12 mg. per liter) potassium ethyl xanthate solution in a Fagergren laboratory-type flotation machine.

Samples taken at approximately 10 minute intervals up to a total of 45 minutes of aeration showed no change in the optical density readings. This indicates that the decomposition of xanthate by oxidation is extremely slow and hence negligible in the following work.

Effect of Alkali.—The effect of alkali on the absorption spectrum of potassium ethyl xanthate solution was tested at *p*H values of approximately 6, 11 and 12; no change in the spectrum was noted. It was also shown that the addition of alkali to a xanthate solution stabilizes the compound to a large extent. In one experiment a solution containing approximately 3.1×10^{-5} mole per liter (5 mg. per liter) of potassium ethyl xanthate solution was left in volumetric flasks at *p*H 6.5 and 10.8 for a period of 8 days. The former solution at *p*H 6.5 showd 75% decomposition, that at *p*H 10.8 only 25%.

Effect of Acid. 1. Between *p*H 2.68–4.71.—In this *p*H range mixing was achieved by manual shaking in a 100-ml. volumetric flask. One milliliter of acid (0.1 and 0.2 *M* hydrochloric or 1 *M* acetic) was added to a flask which contained 100 ml. of 6.2×10^{-5} mole per liter (10 mg. per liter) potassium ethyl xanthate solution, and the mixture was

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[1] H. von Halban and A. Kirsch, *Z. physik. Chem.*, **82**, 325 (1913).

[2] H. von Halban and W. Hecht, *Z. Elektrochem.*, **24**, 65 (1918).

[3] C. V. King and E. Dublon, THIS JOURNAL, **54**, 2177 (1932).

[4] A. Chatenever and C. V. King, *ibid.*, **71**, 3587 (1949).

[5] M. L. Schochet and C. V. King, *ibid.*, **77**, 4745 (1955).

[6] M. A. Cook and J. C. Nixon, *J. Phys. Chem.*, **54**, 445 (1950).

[7] H. Hagihara, *Bull. Kobyashi Inst. Phys. Research, Japan*, **4**, 30 (1954).

[8] C. H. G. Bushell and M. Malnarich, *Trans. AIME*, **205**, 734 (1956).

[9] L. S. Foster, *Utah Eng. Exp. St. T. P.*, **5** (1929).

[10] T. C. Taylor and A. F. Knoll, *Trans. AIME*, **112**, 395 (1934).

shaken vigorously for 1 minute. The resulting solution was transferred to a quartz cuvette and the optical density was recorded at suitable time intervals. The results are plotted in Fig. 1. As seen in the figure, when the logarithm of optical density was plotted against time, straight lines were obtained, the slopes of which increased with decreasing pH. Between pH 3.43 and 4.71, however, when hydrochloric acid was used to regulate the acidity of the solution, the pH increased with the reaction and hence the rate decreased with time. Thus, when the logarithm of optical density was plotted against time, a straight line relationship was not obtained. The pH of the solution, therefore, was kept constant by using buffer solutions containing 0.01 M acetic acid, with various added amounts of sodium acetate to give the desired pH values.

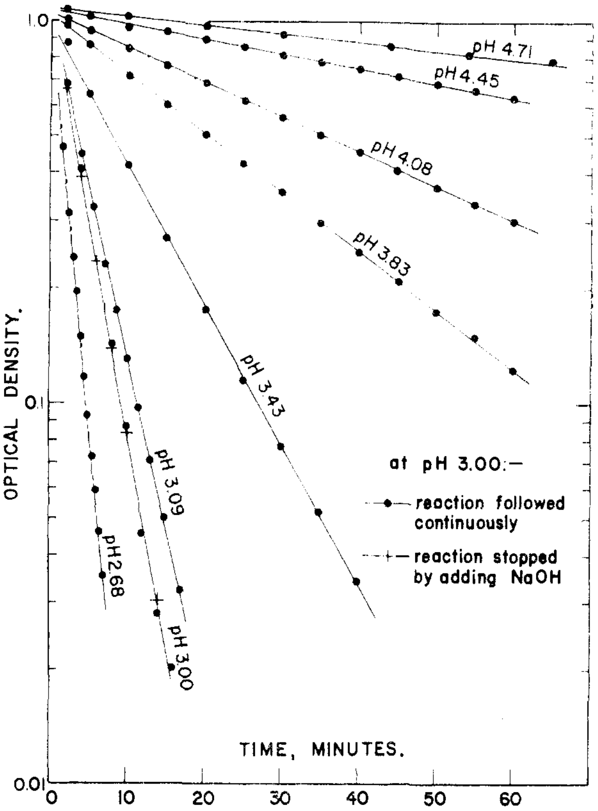

Fig. 1.—Decomposition of potassium ethyl xanthate in the pH range 2.68–4.71.

An absorption spectrum was taken on one of the above solutions after the decomposition was complete. No absorption peak was observed in the wave length range of 220–350 mμ. Restoration of the pH of this solution to 6.5 by addition of sodium hydroxide did not bring back the absorption peak at 301 mμ, indicating that no reverse reaction is possible after the decomposition is complete.

It was noticed that the decomposition reaction was halted when a sufficient amount of alkali was added to the acidified potassium ethyl xanthate solution. Two series of tests were made at pH 3.0 to ascertain the difference between the two cases—first, following the reaction continuously in the cuvette and, secondly, stopping the reaction at suitable time intervals by the addition of alkali. The curve for pH 3.00 (Fig. 1) which gives the results of both tests, indicates that there is no noticeable difference in the results. This fact mutually confirms the validity of the experimental techniques used by von Halban and Hecht[2] and by the present authors.

It is rather interesting to note here that, if potassium ethyl xanthate is precipitated as cupro-xanthate, the yellow color of the precipitate is not re-dissolved by increase in acidity, *i.e.*, precipitation as copper salt seems to stabilize xanthate against the acid pH.

In the previous tests hydrogen ion concentration was kept constant either by using small amounts of xanthate as compared with the hydrogen ion concentration or by using a buffer solution. To test the effect of the interaction of xanthate and hydrogen ions on the rate of decomposition, the following tests were made. In one test approximately equal concentrations of hydrogen and xanthate ions (1.42 $\times 10^{-3}$ mole of hydrochloric acid and 10^{-3} mole of xanthate per liter) were mixed, and the decomposition was followed continuously by noting the change in pH with time, using a Beckman Model G pH meter. In a second test eight flasks containing the same initial hydrogen and xanthate ion concentrations were neutralized with sodium hydroxide at various indicated times, and their xanthate concentrations were determined from optical density measurements. The results of both tests are given in Table I. It is apparent that continuous change occurs both in hydrogen and xanthate ion concentrations.

TABLE I

DECOMPOSITION OF POTASSIUM ETHYL XANTHATE BY HYDROCHLORIC ACID

Time, min.	pH	Xanthate concn., mole/l.
0	. .	1.00×10^{-3}
2	2.99	5.98×10^{-4}
5	3.15	3.38×10^{-4}
10	3.24	1.60×10^{-4}
15	3.29	8.80×10^{-5}
20	3.31	5.00×10^{-5}
25	3.32	3.09×10^{-5}
30	3.33	1.92×10^{-5}
35	3.34	1.17×10^{-5}

2. Between pH 0.10–2.70.—The previous experiment at pH 2.68 (Fig. 1) indicates that further decrease in the pH results in extremely rapid decomposition. This necessitates a procedure for rapid mixing of the solutions in order to measure the optical density within a few seconds after mixing.

An apparatus described by Beers and Sizer[11] was simplified for use in the stated pH range. Two 2-ml. syringes, xanthate solution in one and acid in the other, were fixed in a parallel position on a lucite stand and were connected through plastic tubing to a glass T-tube, where the mixing was effected. The mixed solution was introduced directly into the cuvette through a glass U-tube, which was painted black to shield against light leakage into the cell compartment of the spectrophotometer through the tube opening. A plunger guide enabled the syringe plungers to deliver the solutions at the same rate.

In the pH range from 1.40 to 2.70, potassium ethyl xanthate solution (1.25 $\times 10^{-4}$ mole per liter or 20 mg. per liter) was used in one syringe and hydrochloric acid solutions in the other. Tests were repeated three times at each pH. The results are plotted in Fig. 2. For solutions of lower pH, the optical density at zero time became so low that it was necessary to use a stronger xanthate solution (6.25 $\times 10^{-4}$ mole per liter, or 100 mg. per liter) in order to obtain a sufficient number of points along each line. The results are given in Fig. 3. As shown in both Figs. 2 and 3, the reproducibility of the results, using this apparatus, seems to be quite satisfactory. Furthermore a linear relationship was also obtained between the logarithm of optical density and time for each pH.

Discussion

In the present discussion the decomposition of potassium ethyl xanthate in an acidified aqueous solution is assumed to take place according to

$$H^+ + X^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} HX \xrightarrow{k_3} ROH + CS_2 \qquad (1)$$

Then in general the rate equations for xanthate, xanthic acid and carbon disulfide may be expressed by the relations

$$\frac{d(X^-)}{dt} = -k_1(H^+)(X^-) + k_2(HX) \qquad (2)$$

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[11] R. F. Beers, Jr., and I. W. Sizer, *Anal. Chem.*, **25**, 1137 (1953).

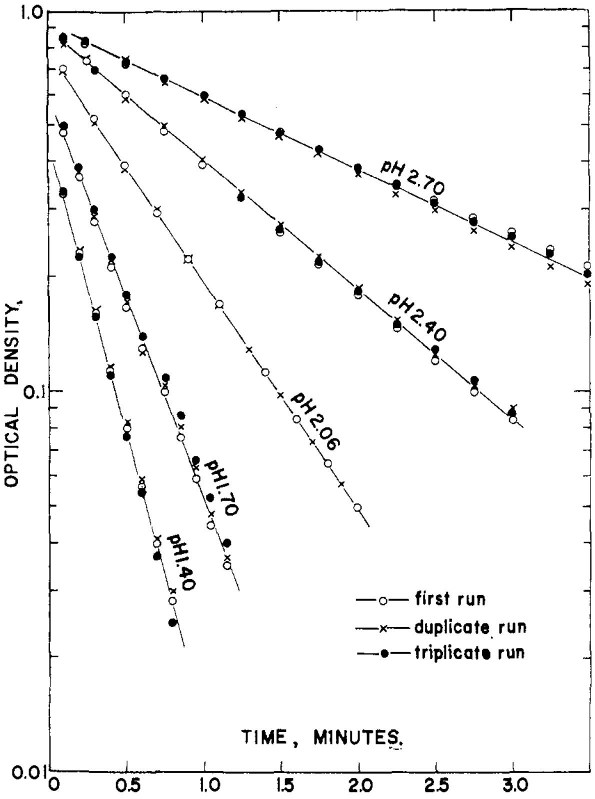

Fig. 2.—Decomposition of potassium ethyl xanthate in the *p*H range of 1.40-2.70.

$$\frac{\mathrm{d(HX)}}{\mathrm{d}t} = k_1(\mathrm{H}^+)(\mathrm{X}^-) - k_2(\mathrm{HX}) - k_3(\mathrm{HX}) \quad (3)$$

$$\frac{\mathrm{d(CS_2)}}{\mathrm{d}t} = k_3(\mathrm{HX}) \quad (4)$$

The above equations, however, may be greatly simplified if the assumption is made that xanthate ion and xanthic acid are in equilibrium during the decomposition and that the rate-determining step in equation 1 is the monomolecular decomposition of xanthic acid. This assumption is probably quite reasonable, since reactions involving ionic combination are known to be extremely rapid.[12] The validity of the assumption is established with the following discussion.

Since the optical density at the wave length of 301 mμ measures the total concentration of xanthate and xanthic acid, equations 2 and 3 are combined to give another expression

$$\frac{\mathrm{d(X^-)}}{\mathrm{d}t} + \frac{\mathrm{d(HX)}}{\mathrm{d}t} = \frac{\mathrm{d(X^- + HX)}}{\mathrm{d}t} = -k_3(\mathrm{HX}) \quad (5)$$

By using the dissociation constant of xanthic acid, equation 5 can be rewritten in terms of the total concentration, *C*, as follows:

$$\frac{\mathrm{d}C}{\mathrm{d}t} = -k_3C_1 = -\frac{k_3}{1 + K/(\mathrm{H}^+)}\,C$$

or

$$-\frac{\mathrm{d}\ln C}{\mathrm{d}t} = \frac{k_3}{1 + K/(\mathrm{H}^+)} \equiv \kappa \quad (6)$$

where C_1 is the concentration of xanthic acid. Upon integration of equation 6

$$\log\frac{(C)_1}{(C)_2} = \frac{(\text{Optical density})_1}{(\text{Optical density})_2} = \frac{\kappa}{2.303}\,(t_2 - t_1) \quad (7)$$

Therefore, $\kappa/2.303$ may be identified as the slopes of the various linear plots which are presented in Figs. 1, 2 and 3.

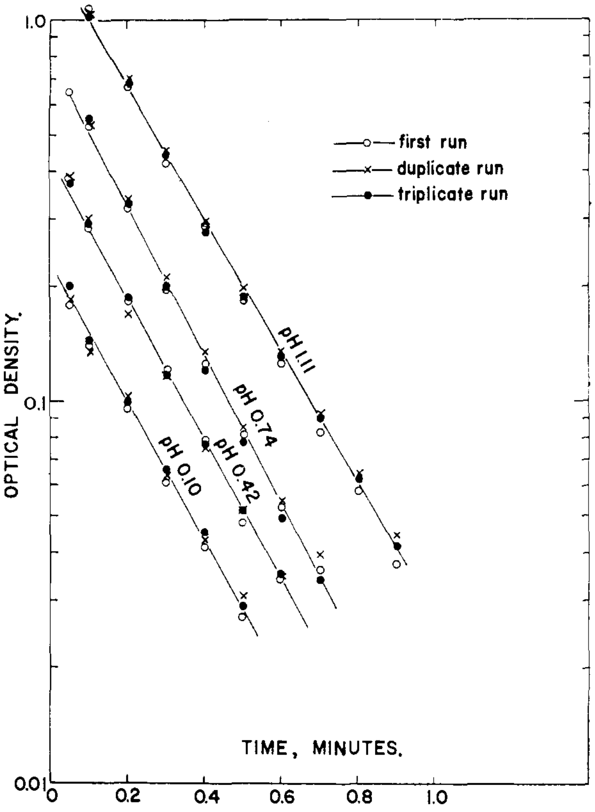

Fig. 3.—Decomposition of potassium ethyl xanthate in the *p*H range of 0.10-1.11.

The following approximation leads to an important relation

(A) When $(\mathrm{H}^+) \ll K \quad \kappa \cong \frac{k_3}{K}(\mathrm{H}^+)$

$$\text{or } \log\kappa = \log\frac{k_3}{K} - p\mathrm{H} \quad (8)$$

(B) When $(\mathrm{H}^+) \gg K \quad \kappa \cong k_3$ (9)

This indicates that, when log κ is plotted against *p*H, under conditions (A), a straight line with a slope of -1 should result. If condition (B) pertains, log κ would be independent of *p*H.

The values of κ have been calculated from Figs. 1, 2 and 3, and in Fig. 4 the logarithm of κ is plotted against the corresponding *p*H. As will be seen from this figure, condition (A) is satisfied at *p*H values above 2.7. The slope of the line in this region was calculated from the seven points obtained from Fig. 1. It is -0.986 with a standard deviation of ± 0.005, from which log k_3/K was calculated to be 2.33 ± 0.019, or $k_3/K = 216 \pm 1.8$. Condition (B) may be applied to the *p*H range below 0.74 and, since $\kappa = k_3$, the average values of κ at *p*H 0.74, 0.42 and 0.10 may be used to calculate the monomolecular decomposition rate constant, k_3. Thus the value of k_3 becomes 4.3 ± 0.21 minutes^{-1}. The dissociation constant for xanthic acid, *K*, would then be calculated from the constants, k_3/K and k_3, and this value of *K* was found to be 0.020 ± 0.001. Graphically, the intersection of the two lines (A) and (B) also corresponds to $-\log K$, which is 1.70 on the *p*H scale. The results presented in Fig. 4 have therefore demonstrated that our initial assumption of the mechanism of the decomposition reaction, which was assumed to take place according to equation 1, is essentially correct.

With regard to the dissociation constant of xanthic acid, von Halban and Hecht[2] report a value of 0.030, Hantzsch and Bucirius,[13] 0.028 from conductivity measurement, King and Dublon,[3] 0.031, and Cook and Nixon,[6] 0.007. The present value, 0.020, although slightly lower than the first three, checks well with the previously reported values. It

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(12) M. Eigen, *Disc. Faraday Soc.*, **17**, 194 (1954).

(13) A. Hantzsch and W. Bucirius, *Ber.*, **59**, 793 (1926).

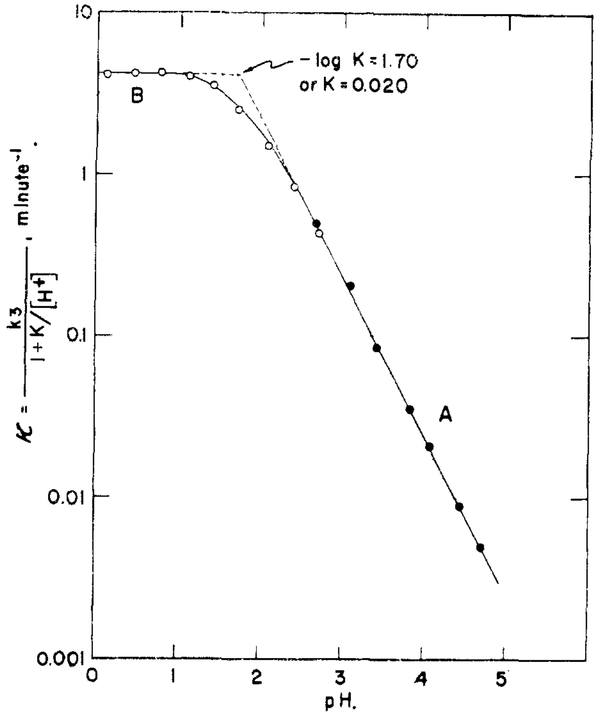

Fig. 4.—κ as a function of pH.

is our feeling, however, that the present method has an advantage over others in that a spectrophotometer measures xanthate and xanthic acid concentrations directly. The methods used by von Halban and Hecht[2] and Hantzsch and Bucirius[13] could be subject to some error due to the presence of H_2S and HS- as pointed out by Cook and Nixon.[6] The carbon disulfide evolution method of King and Dublon[3] may receive some contribution to the total pressure from the resulting alcohol and xanthic acid. It should be noted, however, that the present investigation is in good agreement with the work of Chatenever and King,[4] their value for log k being 2.38 at 25° as compared with our value of log $k_3/K = 2.33$ at 23.5°. In view of equation 4, which may be rewritten as

$$\frac{d\,(CS_2)}{dt} = k_3(HX) = \frac{k_3}{K}(H^+)(X^-) \qquad (10)$$

Equation 10 is equivalent to equation 1 as given by King and Dublon[3] on p. 2178 of their article, which apparently indicates that their k may be identified as k_3/K according to our interpretation.

Acknowledgments.—The authors are extremely grateful to Professor Carl Wagner of the Department of Metallurgy, Massachusetts Institute of Technology, for his valuable suggestions regarding the theoretical interpretation of this investigation. We wish to thank Professors A. M. Gaudin and P. L. deBruyn for their interest and for making available certain laboratory facilities at M.I.T. to enable one of us (I.I.) to perform a part of this investigation. The authors are also indebted to Dr. F. F. Aplan (M.I.T.) for his encouragement and for his interest shown in the publishing of this work.

MINNEAPOLIS 14, MINN.

[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Kinetics of the Decomposition of Sodium *p*-Toluenesulfonylacetate in Water–Ethylene Glycol and Water–Dioxane Mixtures

BY DONALD J. O'CONNOR AND FRANK H. VERHOEK

RECEIVED JULY 10, 1957

The reaction of sodium *p*-toluenesulfonylacetate to form methyl *p*-tolyl sulfone and sodium bicarbonate has been studied in water–ethylene glycol mixtures at 75, 85 and 95° and in water–dioxane mixtures at 75 and 85°. The reaction is first order in all cases, increasing in rate with increase in organic component of the solvent, with small changes in activation energy and frequency factor. The reaction has been shown to be a decarboxylation of the anion by studies on the acid in water at 95°; the decomposition of this substance is of the one-half order, corresponding to an incomplete dissociation of the acid with a kinetically determined ionization constant of 1.6×10^{-4}. The results are compared with other first-order decarboxylations in the same solvents.

The decarboxylation of alkali metal salts of α-aryl sulfonyl acetic acids, forming methyl α-aryl sulfones, on heating in alkaline solution was reported by Otto.[1] The present paper reports a kinetic study of the decomposition of *p*-toluenesulfonylacetic acid and its sodium salt in water and ethylene glycol, and in mixtures of water and ethylene glycol and water and dioxane. The results show that the decomposition is first order in the anion of the acid, and so is similar to the decarboxylation of trichloroacetic,[2] trifluoroacetic[3] and trinitrobenzoic[4] acids.

Experimental

For the preparation of *p*-toluenesulfonylacetic acid, sodium *p*-toluenemercaptoacetate was first prepared from thiocresol and monochloroacetic acid in alkaline solution, following Auwers and Thies.[5] Free *p*-toluenemercaptoacetic acid was formed by the addition of hydrochloric acid, and recrystallized from water and twice from benzene. The melting point was 93–94°; the yield 90%. The purified *p*-toluenemercaptoacetic acid, dissolved in glacial acetic acid, was oxidized by the slow addition of 30% hydrogen peroxide, as in the procedure of Siebert and Fromm.[6] Most of the glacial acetic acid was distilled off *in vacuo*, and the residue poured into water and recrystallized rapidly. Two further recrystallizations from benzene gave white crystals of *p*-toluenesulfonylacetic acid. The melting point was 117.0–117.5°; the neutral equivalent 214.1 (theoretical 214.2); the yield 80%. Sodium *p*-toluenesulfonylacetate was prepared by mixing equivalent quantities of the acid and sodium hydroxide in alcohol solution. The salt precipitated

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

(2) F. H. Verhoek, THIS JOURNAL, **56**, 571 (1934); **67**, 1062 (1945); G. A. Hall and F. H. Verhoek, *ibid.*, **69**, 613 (1947).

(3) I. Auerbach, F. H. Verhoek and A. L. Henne, *ibid.*, **72**, 299 (1950).

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

(5) K. Auwers and W. Thies, *Ber.*, **53**, 2285 (1920).

(6) E. Siebert and E. Fromm, **55**, *ibid.*, 1014 (1922).