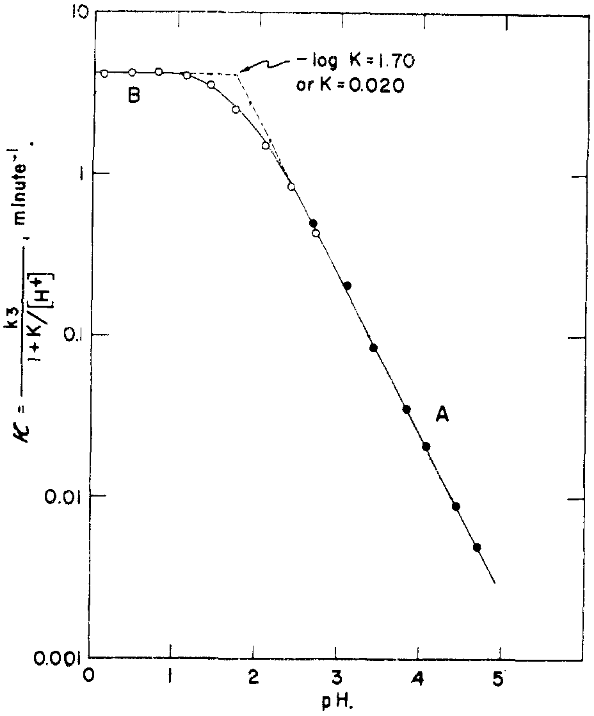

Fig. 4.—κ as a function of *p*H.

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 $k_1/K = 2.33$ at 23.5°. In view of equation 4, which may be rewritten as

$$\frac{d\,(CS_2)}{dt} = k_1(HX) = \frac{k_1}{K}(H^+)(X^-) \qquad (10)$$

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_1/K according to our interpretation.

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[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

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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^{-3}. 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).

immediately. It was recrystallized from alcohol and stored in a desiccator.

Ethylene glycol was prepared for use by drying over Drierite and distilling at 1.7 mm. through a 40 cm. column. The middle half was collected and stored under nitrogen. Analysis with Fischer reagent showed less than 0.05% water. Dioxane was purified according to Fieser's description[7] of the method of Hess and Frahm. The middle three-fifths (b.p. 101.1–101.2°) was collected and stored under nitrogen. Weighed amounts of one of the above solvents were mixed with weighed amounts of water in order to prepare the solvent mixtures.

The reacting solutions were made up by weight, and 10-ml. samples pipetted into individual reaction flasks, which were then immersed in the constant temperature baths. Twenty minutes to one-half hour was allowed to attain temperature equilibrium. The reaction was stopped by plunging a reaction flask into an ice-bath, the time at which the first flask was removed being taken as zero time. In the study of decomposition of the sodium salt, standard hydrochloric acid was added to the cooled flask, and nitrogen bubbled through for 10 minutes to remove carbon dioxide. The excess acid was titrated to a phenolphthalein end-point with standard sodium hydroxide from a micro buret. This titration permits the calculation of the amount of bicarbonate formed; subtraction of this quantity from the known starting concentration gives the amount of salt undecomposed. For the decomposition of free *p*-toluenesulfonylacetic acid, acidification with hydrochloric acid is unnecessary, and the solutions were titrated directly with base after bubbling with nitrogen to remove carbon dioxide.

The experiments were carried out at 75, 85 and 95° with solutions containing ethylene glycol, and at 75 and 85° with solutions containing dioxane.

Results

The reaction as reported by Otto[1] was verified by refluxing for six days an aqueous alkaline solution containing a weighed quantity of sodium *p*-toluenesulfonylacetate and extracting with ether. A quantity of methyl *p*-tolyl sulfone (m.p. 85.5–86.2°; lit. 86–87°) corresponding to 97% reaction according to equation 1 was obtained.

$$CH_3C_6H_4SO_2CH_2COO^- + H_2O \longrightarrow CH_3C_6H_4SO_2CH_3 + HCO_3^- \quad (1)$$

The first-order course of the decomposition of sodium *p*-toluenesulfonyl acetate in water and in 39.9% ethylene glycol was determined by special experiments for which the concentration of unreacted salt was plotted against the time. The tangents dc/dt were then measured at various concentrations and log $(-dc/dt)$ plotted against log c; straight lines of unit slope were obtained in both cases. For all other experiments involving the sodium salt, straight lines were obtained when log c was plotted against the time, confirming the first-order course. All experiments at 95° were carried out to 75–80% completion; at the lower temperatures the reactions were stopped farther from completion.

Since bicarbonate is formed during the reaction, it is necessary to see whether the rate is affected by the increasing alkalinity. Accordingly an experiment was carried out in which the *p*H was raised by adding the strong base sodium hydroxide equivalent to 10% of the decomposing substance. The reaction followed a first-order course at the same rate as in the absence of added base. Similarly, addition of pyridine had no effect upon the order or rate.

The values of the first-order velocity constants obtained are given in Table I. The activation energies, from data over a small temperature range, are not precisely determined; however, for the experiments at three temperatures, excellent straight lines were obtained in all cases for which activation energies are recorded, on plotting log k against $1/T$.

TABLE I

VELOCITY CONSTANTS FOR THE DECARBOXYLATION OF SODIUM *p*-TOLUENESULFONYLACETATE IN WATER–ETHYLENE GLYCOL AND WATER–DIOXANE MIXTURES

Wt. % organic solvent Ethylene glycol	Starting concn. (mole/l. × 10^2)		$k \times 10^2$ (hr.$^{-1}$)		Activation energy, kcal.
		75°	85°	95°	
0	9.07	0.186	0.790	2.97	35.4
0	9.14	.204	.806	3.07	34.7
0	9.24	..	..	3.02[a]	..
0	8.92	..	..	3.01[b]	..
0	5.05	..	..	3.01	..
0	0.949	.223	.775	2.86	32.6
20.5	9.16	.242	1.01	4.02	35.9
20.5	0.939	.223	0.899	3.25	34.2
39.9	9.16	.383	1.47	5.33	33.7
59.2	8.42	.495	2.15	8.19	35.8
59.2	0.879	.433	1.73	7.14	35.8
59.2	0.945	.433	1.98	6.37	..
79.6	9.05	.937	3.61	13.28	33.9
79.6	0.916	.720	2.48	11.39	..
100.0	9.22	1.732	6.47	23.75	33.4
100.0	0.887	1.54	4.24	21.19	..
Dioxane					
21.4	9.35	0.383	1.603	..	35.6
40.0	9.46	0.967	4.05	..	35.6
60.0	9.59	2.69	9.36	..	31.0
60.1	9.51	2.31	8.45	..	32.2
79.7	9.77	5.89	22.2	..	32.9

[a] Solution was 0.01 molar in NaOH. [b] Solution was 0.008 molar in pyridine.

The behavior of free *p*-toluenesulfonylacetic acid was investigated in water, ethylene glycol and dioxane solutions. In dioxane solution no decomposition could be detected. In ethylene glycol there was a rapid esterification; rough quantitative estimates showed that all of the acid which disappeared could be accounted for as ester. In water solution the half-life of the decomposition of the free acid was 6–7 times as great as that for the sodium salt, and the decomposition was found to be one-half order. A one-half order law is expected if the acid is slightly dissociated and the decomposition is determined by the concentration of the anion of the acid, while the undissociated acid is stable, for then eq. (2) should be obeyed

$$-\frac{d[HA]}{dt} = k[A^-] = kK^{1/2}[HA]^{1/2} \quad (2)$$

Here K is the dissociation constant of the acid and [HA] may be considered its total concentration. From the initial slope of the concentration–time curve and the initial concentration, and using the value of k from the experiments with the sodium salt, the value of K at 95° was determined as 1.6×10^{-3}. If this value is used with the slope of a plot of $\sqrt{[HA]}$ against t, obtained from the integrated form of equation 2, k is determined to be

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[7] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, p. 369.

TABLE II

KINETIC DATA FOR THE DECARBOXYLATION OF SODIUM TRICHLOROACETATE, SODIUM *p*-TOLUENESULFONYLACETATE AND TRINITROBENZOATE ION IN VARIOUS SOLVENTS

	CCl_3COONa			$CH_3C_6H_4SO_2CH_2COONa$			$(NO_2)_3C_6H_2COO^-$	
	Water[a]	Ethylene glycol[b]	83% Dioxane[c]	Water	Ethylene glycol	79.7% Dioxane	Water[d]	80% dioxane[d]
k at 75°, sec.$^{-1}$ × 10^5	3.55	4.09	138	0.0542	0.481	1.64	2.30	2450
E(kcal.)	35.9	31.3	27.6	34.9	33.4	32.9	35.8	23.8
log s	18.1	15.3	14.5	15.7	15.7	15.9	17.9	13.3

[a] Reference 2. [b] Reference 3. [c] E. J. Salmi and R. S. Korte, *Suomen Kemistilehti* 18, 28 (1945). [d] Reference 4.

2.95×10^{-2} hr.$^{-1}$, in agreement with the value for the salt. A direct measurement of K at room temperature from the pH at half neutralization gave 2.4×10^{-3} in agreement with the kinetic value at the higher temperature.

Discussion

The data show that the decomposition rate is determined by the concentration of the *p*-toluenesulfonylacetate ion. *p*-Toluenesulfonylacetic acid may thus be classified with the unimolecular group of decarboxylating acids,[8,9] with the rate-determining step

$$CH_3C_6H_4SO_2CH_2COO^- \longrightarrow CH_3C_6H_4SO_2CH^- + CO_2 \quad (3)$$

followed by a reaction with a proton to form methyl *p*-tolyl sulfone as the final product, though the data do not distinguish between this mechanism and a pseudo-unimolecular reaction involving the ion and the solvent.

It will be observed in the data for water–ethylene glycol solutions in Table I that the velocity constant in solutions of starting concentration 9×10^{-3} molar are less than those in 9×10^{-2} molar solutions. No explanation is at present available for this result and it must be provisionally classified as a "salt effect." It should be noted that this behavior is opposite to that observed with salts of other decarboxylating acids,[2] for which concentrated solutions show smaller velocity constants than dilute, especially in the presence of nonaqueous solvents. In those cases, the change in rate constant has been explained as a shift in the degree of dissociation of the salt with increasing dilution, but this explanation will not apply to the opposite trend observed here. This does not eliminate the possibility, however, that sodium *p*-toluenesulfonylacetate is partly associated into ion pairs in the solvents of lower dielectric constant for both solvent mixtures, so that the values reported in Table I are actually smaller than those which would be obtained if the true anion concentration could be calculated.

The data in Table I show that there is an increase in velocity constant as the organic component in the solvent is increased. This has been commonly found in other cases in which first-order decarboxylations have been investigated in mixed solvents.[2,4] In the other cases this increase in rate has been accompanied by a large decrease in activation energy and a decrease in the frequency factor in the Arrhenius equation. This is shown, for example, in the data of Table II, which compares *p*-toluenesulfonylacetate ion with trichloroacetate and trinitrobenzoate ions, which have been studied in the same solvents. For the *p*-toluenesulfonylacetate ion, however, the change in both activation energy and frequency factor with addition of organic solvent is small. *p*-Toluenesulfonylacetate ion thus shows an inertness to solvent effects, compared to the other anions.

Another interesting feature of the reaction studied here is that if the velocity constants at 75 or at 85° are plotted against the dielectric constants of the solvent mixtures, the points for both solvent mixtures lie on the same curve. It is not known whether this relationship will hold for other solvent mixtures.

For trichloroacetate and trinitrobenzoate ions, the increase in rate with increase in organic solvent content was attributed to the fact that the ions were highly solvated in water and became progressively less so as organic material was added to the solvent. Reaction was presumed to require desolvation, a process requiring activation energy, so that both the activation energy and the entropy of activation would be higher in the solvating, high-water-content, solvents. Schenkel and Schenkel-Rudin[8] suggested further that the solvation occurred by hydrogen-bonding with the oxygens of the carboxyl group, causing the carbon atom of that group to become more positive, and hindering the removal of the pair of electrons from the carbon of that group by the α-carbon atom. The simplest explanation for the behavior of *p*-toluenesulfonacetate ion is that it is not appreciably solvated even in water and hence remains unaffected by changing solvent. Another attractive possibility is that the *p*-toluenesulfonylacetate ion has two centers for solvation, by hydrogen bonding: the oxygens of the carboxyl group and those of the sulfone group. Solvation of the carboxyl group hinders the reaction as in the other cases, but hydrogen bonding to the sulfone oxygen aids the reaction by attracting electrons to the α-carbon. Thus change in hydrogen bonding ability of the solvent leads to competing influences which appear nearly to cancel out to give no total effect. Solvation at two centers offers no help in explaining the constancy in log s.

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

[9] B. R. Brown, *Quart. Rev.*, **5**, 131 (1951).