

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WASHINGTON SQUARE
COLLEGE, NEW YORK UNIVERSITY]

THE RATE OF DECOMPOSITION OF XANTHIC ACID

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Introduction

It was suggested by Brönsted in 1925 that a study of the kinetics of the decomposition of the xanthic acids in aqueous solution would be valuable, and preliminary experiments were carried out by one of the present writers (C. V. K.). These experiments were discontinued because no convenient method was available for measuring the rates accurately.

The methyl and ethylxanthic acids are neither as strong as hydrochloric nor as weak as the ordinary organic acids, but are somewhat stronger than dichloroacetic acid. Both primary and secondary salt effects influence their decomposition rates, in the acid solution alone and in buffer solutions. Accurate measurements of the rates were made and the results were analyzed by v. Halban and his co-workers before the development of salt effect theory; consequently the importance of both types of salt effect was neglected entirely.

The rate of decomposition was first studied in detail by v. Halban and Kirsch,¹ who prepared the free methyl and ethylxanthic acids, found a method of stabilizing them, and studied their decomposition in a number of solvents. Roughly, the rate increases with the polarity of the solvent; in solvents of low dielectric constant it is autocatalytic because of the alcohol formed, but this is not true in alcohol itself or in water.

V. Halban and Hecht² published the results of an extensive study of the rates in aqueous solution. Potassium ethyl or methyl xanthate solutions were mixed with hydrochloric acid in known concentrations and the solutions analyzed at suitable time intervals; although the reaction was very rapid, the measurements were carried out with such precision, over such a wide concentration range and to such low ionic strengths that in some respects they are ideal for reinterpretation on the basis of the newer theories.

It was assumed that the reaction was a unimolecular decomposition of undissociated xanthic acid, although v. Halban recognized that this is kinetically identical with a bimolecular reaction between the hydrogen and xanthate ions. The unimolecular " k " increases and reaches a maximum value as the hydrochloric acid concentration is increased; from the ratio of the rate constants the dissociation constants were calculated. The values obtained were 0.030 for ethylxanthic acid, 0.034 for methylxanthic

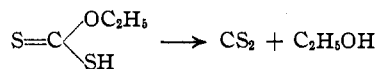
¹ V. Halban and Kirsch, *Z. physik. Chem.*, **82**, 325 (1913).

² V. Halban and Hecht, *Z. Elektrochem.*, **24**, 65 (1918).

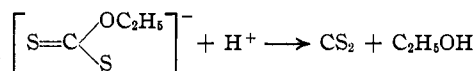
acid; we shall show later that these are correct for zero ionic strength but not for finite salt concentrations.

Experimental

Our own experiments were carried out with ethylxanthic acid in acetic acid-sodium acetate and aniline-aniline hydrochloride buffers. Since the xanthic acid is so strong, no appreciable amount of undissociated acid will remain in these buffers, and salt effect on this equilibrium can be neglected. The reaction may take place by either of the following mechanisms



or



but since the concentration of undissociated xanthic acid is controlled by the xanthate and hydrogen-ion concentrations, these lead to the same kinetic equation

$$\frac{dx}{dt} = k C_{\text{H}^+} C_{\text{X}^-} \frac{f_1^2}{f_0} \quad (1)$$

where X^- is used for the xanthate ion, f_1 and f_0 are activity coefficients of the univalent ions and neutral reaction complex.

Since the hydrogen-ion concentration of an acetic acid-acetate buffer is given by

$$C_{\text{H}^+} = K_{0, \text{HAo}} \frac{C_{\text{HAo}} f_0}{C_{\text{Ae}^-} f_1^2}$$

the final rate equation in such a buffer becomes with close approximation

$$k = \frac{2.3}{K_0'} \left[\frac{a+c}{b-a} \log \frac{a}{a-x} - \frac{b+c}{b-a} \log \frac{b}{b-x} \right] \quad (2)$$

where a is initial xanthate concentration, b is initial acetic acid concentration, c is initial acetate-ion concentration; this is formally identical with the classical rate expression where salt effects are neglected.

In the aniline-anilinium ion buffer, however

$$C_{\text{H}^+} = K_{0, \text{AnH}^+} \frac{C_{\text{AnH}^+}}{C_{\text{An}}} \frac{1}{f_0}$$

and when this is substituted in (1) the activity coefficients do not cancel. Consequently, when the classical expression (2) is used for calculating the rates in these buffers, we shall expect that as the ionic strength is increased, the values of k will diminish in accordance with the relation³

$$k = k_0 \frac{f_1^2}{f_0^2}$$

³ See Brønsted and Pedersen, *Z. physik. Chem.*, **108**, 185 (1924), for a discussion of salt effects in these buffers.

Potassium xanthate was recrystallized from aqueous alcohol until the fresh solution was neutral to phenolphthalein; the crystals were sucked dry and further dried over sulfuric acid. Standard acetic acid was partially neutralized to prepare buffers. Aniline was distilled three times and weighed amounts dissolved in standard hydrochloric acid for stock solutions.

The reactions were followed by measuring the increase in vapor pressure above the solutions, chiefly due to the carbon disulfide formed, in a modification of the apparatus designed by Brönsted.⁴ After introducing 100 cc. of the buffer solution into the reaction flask, a weighed amount of potassium xanthate in a glass capsule was suspended from a hook in the neck, the neck was sealed off and the entire apparatus was evacuated (while shaking) and sealed. When the pressure reading became constant the xanthate was dropped in and quickly dissolved, and pressure readings taken at frequent intervals. The thermostat was kept at $25 \pm 0.02^\circ$.

Several pressure readings which fell on a smooth curve through all readings were selected to calculate the rate constants. These can be calculated from equation (2) by using pressure readings directly or by calculating and using actual concentrations.

Acetic Acid-Acetate Buffers.—Details of a typical experiment are given in Table I.

TABLE I

INITIAL CONCENTRATIONS: $C_{KX} = 0.015M$, $C_{HAC} = 0.04M$, $C_{NaAc} = 0.01M$

t , min.	x (m. p. l.)	k^a
20	0.00401	253
40	.00625	267
60	.00778	268
92	.00951	270
116	.01048	274
152	.01144	270

Average 267, av. dev., 4.7

^a $K_{0, HAC} = 1.86 \times 10^{-5}$.

Table II summarizes a number of experiments in which the hydrogen-ion concentration was kept approximately the same at the beginning of each experiment, and shows that there is no unusual effect of the undissociated acetic acid. Table III summarizes experiments in which the initial hydrogen-ion concentration was varied, and shows that the values of k are independent of this factor (which is also indicated by the constancy of k in individual experiments, since C_{H^+} decreases considerably during the reaction with the buffer concentrations used). Table IV shows that k is not affected by changing the initial xanthate concentration, although the limitations of the apparatus used made it impossible to vary this over a wide range.

⁴ King, THIS JOURNAL, 50, 2090 (1928).

TABLE II

Initial concentrations			
C_{KX}, M	C_{HAc}	C_{NaAc}	k
0.015	0.04	0.01	271
.015	.05	.0125	255
.015	.05	.0125	266
.015	.10	.025	284
.015	.10	.025	266
.015	.10	.025	279
.015	.10	.025	278
.015	.20	.05	279
.015	.20	.05	262

Av. 271, av. dev., 8

TABLE III

Initial concentrations			
C_{KX}	C_{HAc}	C_{NaAc}	k
0.015	0.05	0.025	278
.015	.05	.025	278
.015	.075	.025	266
.015	.10	.025	278 ^a
.015	.125	.025	262
.015	.15	.025	267

Av. 273, av. dev., 7

^a Average of four experiments.

TABLE IV

C_{KX}	C_{HAc}	C_{NaAc}	k
0.015	0.075	0.025	266
.01	.075	.025	270
.01	.075	.025	275

Av. 270

At higher salt concentrations the activity coefficients do not cancel and equation (2) is no longer valid; this is shown in Table V where the marked diminution of k is evident when sufficient inert salt is added.

TABLE V

C_{KX}	C_{HAc}	C_{NaAc}	C_{KCl}	k
0.015	0.04	0.01	0	271
.015	.10	.025	.2	250
.010	.10	.025	.4	252
.010	.10	.025	.4	260
.015	.04	.01	.5	250
.015	.10	.025	.75	235
.015	.10	.025	1.0	221

Aniline-Anilinium Ion Buffers.—Since the dissociation constant of the anilinium ion is near that of acetic acid⁵ these mixtures give a suitable

⁵ See Brönsted and Duus, *Z. physik. Chem.*, **117**, 299 (1925).

hydrogen-ion concentration. The value of K_{AnH^+} used in calculating the constants in Tables VI and VII may be several per cent. in error for 25° , but not enough to obscure the results. Since the ionic strength decreases during the reaction, and the buffer equilibrium has no positive salt effect to neutralize the negative effect on the reaction, the values of k should increase during each experiment. Actually the decrease in ionic strength was not sufficient in any of our experiments to make this evident. Details of typical experiments are given in Table VI.

TABLE VI

Initial concentrations $C_{\text{KX}} = 0.015 M, C_{\text{AnH}^+} = 0.114 M$ $C_{\text{An}} = 0.036 M$			Initial concentrations $C_{\text{KX}} = 0.015 M, C_{\text{AnH}^+} = 0.0855 M$ $C_{\text{An}} = 0.0195 M$		
t	x	k^a	t	x	k^a
20	0.00345	199	20	0.00430	201
32	.00495	196	32	.00596	198
40	.00578	195	40	.00688	198
56	.00706	187	56	.00840	200
80	.00890	192	80	.01000	200
112	.01060	196	112	.01148	200
176	.01260	198	176	.01322	205
Av. 195			Av. 200		

$$^a K_{\text{AnH}^+} = 2.2 \times 10^{-5}.$$

Table VII summarizes several experiments in which the hydrogen-ion concentration and the ionic strength were varied. It is evident that only the change in ionic strength affects the value of k . At the ionic strength 0.094, $k = 200$, much lower than the average value $k_0 = 271$ obtained from the acetic acid buffers. The sign and magnitude of the salt effect agree well with the predicted.

TABLE VII

C_{KX}	C_{AnH^+}	C_{An}	C_{NaCl}	$\mu(\text{mean})$	k
0.015	0.0855	0.0195	0	0.0939	200
.015	.114	.036		.122	195
.015	.114	.027		.122	192
.015	.114	.019		.122	184
.015	.114	.027	.2	.322	155
.015	.114	.036	.5	.622	129
.015	.0855	.0195	1.0	1.094	105

Analysis of the Data of v. Halban and Hecht.—The measurement of v. Halban and Hecht were all made at 0° , mostly in such dilute solutions that the change in ionic strength during each reaction was considerable. When k is calculated from the classical bimolecular expression

$$\frac{dx}{dt} = k C_{\text{H}^+} C_{\text{X}^-}$$

the changing salt effect causes the values of k to increase during each experiment, as is shown in Table VIII.

TABLE VIII

INITIAL $C_{KX} = a$, INITIAL $C_{HCl} = b$, TEMPERATURE, 0°							
t , min.	v. Halban's Table 2			v. Halban's Table 4			
	$a - x$	$b - x$	k		$a - x$	$b - x$	k
0	0.0144	0.0185	..	0	0.00846	0.01006	..
2.5	.01122	.0153	5.80	13	.00359	.00519	9.38
4	.00956	.0137	6.66	15	.00319	.00479	9.70
5	.00854	.0126	6.75	20	.00242	.00402	10.44
8	.00661	.0107	7.01				

Because of the complication of undissociated acid formation it is impossible in this case to apply the method outlined by Scatchard for reactions in a changing environment.⁶ We have tabulated the initial values of k (bimolecular) for v. Halban's measurements on ethylxanthic acid, and

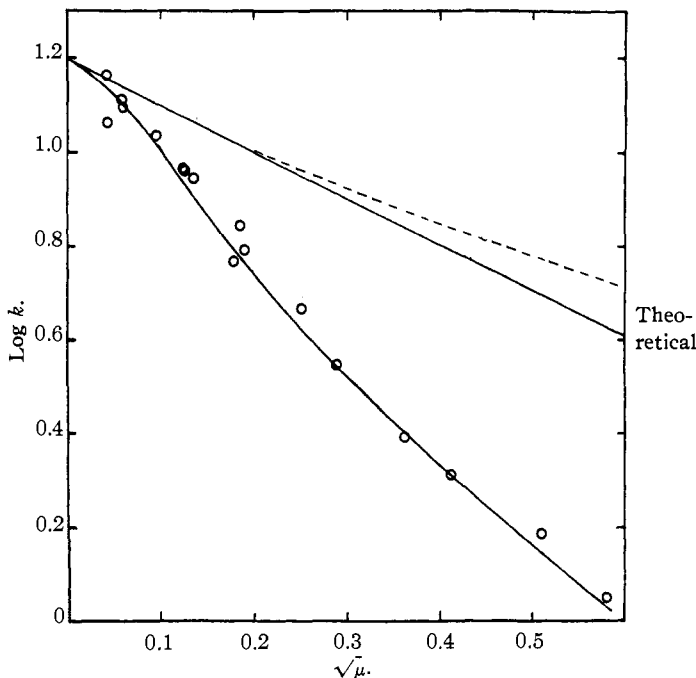


Fig. 1.—Comparison of observed rates with the theoretical for ethylxanthic acid at 0°: theoretical slope, -0.97 .

also the mean values of the ionic strength during each initial measurement (Table IX). In Fig. 1 the values of $\log k$ are plotted against $\sqrt{\mu}$. If we could use the correct ion concentrations to calculate k , the experimental points should approach the theoretical relation

$$\log k = \log k_0 - 0.97 \sqrt{\mu} \text{ (at } 0^\circ \text{)}$$

⁶ Scatchard, THIS JOURNAL, 52, 52 (1930).

as the ionic strength decreases, and deviations from this should be positive rather than negative, as indicated by the dotted line of Fig. 1. On the other hand, the change in dissociation constant with ionic strength at low concentrations is given by

$$\log K = \log K_0 + 0.97 \sqrt{\mu} \quad (3)$$

and deviations from this with increasing ionic strength will be negative. These two relations can now be used to evaluate \bar{K} .

TABLE IX
BIMOLECULAR "CONSTANTS" FOR ETHYLBXANTHIC ACID AT 0°

v. Halban's table	$\sqrt{\mu}$	k	v. Halban's table	$\sqrt{\mu}$	k
9	0.0409	14.55 ^a	1	0.185	7.03
9	.0434	11.54	39	.190	6.21
8	.0570	12.99	37	.251	4.67
7	.0605	12.59	31	.290	3.50
6	.0953	10.86	38	.364	2.46
4	.126	9.38	35	.41	2.07
5	.127	9.20	40	.51	1.52
3	.136	8.76	36	.58	1.14
2	.177	5.80	32	.71	0.77

^a "Interval constant" from the last two measurements.

For equal concentrations of H^+ and X^- , the k we have calculated is given by

$$k = \frac{1}{at} \frac{x}{(a-x)}$$

But if m is the average concentration of undissociated xanthic acid during the measurement, the rate is more correctly given by

$$k_w = \frac{1}{(a-m)t} \frac{x}{(a-m-x)}$$

and as $x \doteq 0$

$$\frac{k_w}{k} = \frac{a^2}{(a-m)^2}$$

Since $2a-m = \mu$, this gives finally

$$m = \mu \frac{\sqrt{k_w/k} - 1}{\sqrt{k_w/k} + 1} \quad (4)$$

The dissociation constant can be expressed by

$$K = \frac{(\mu - m)^2}{4m} \quad (5)$$

and substituting (4) in (5) gives

$$K = \frac{\mu}{k_w/k - 1} \quad (6)$$

By a series of trials, equation (6) was used to draw the curve shown in Fig. 1 through the experimental points. The values of k_w/k used are given in Table X, and Fig. 2 shows that these values make equation (3)

TABLE X

$\sqrt{\mu}$	k_w/k	K
0.05	1.071	0.035
.1	1.26	.038
.2	1.82	.049
.3	2.40	.064
.4	3.02	.079
.5	3.63	.095

The values of K above $\sqrt{\mu} = 0.2$ are actually too high, but are used in extrapolating to $\mu = 0$.

valid. The extrapolated value for K_0 becomes 0.031, in good agreement with v. Halban's value 0.030. The dotted line in Fig. 2, rather than the solid line, shows the expected course of K with increasing ionic strength; no change in K appears with v. Halban's method of calculation.

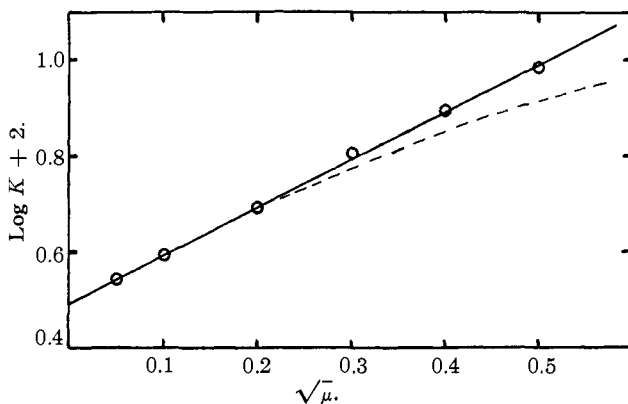


Fig. 2.—Variation in dissociation constant of ethylxanthic acid with ionic strength (see Table X): theoretical slope, +0.97.

Tables XI and XII, Figs. 3 and 4, show the same treatment applied to the measurements on methylxanthic acid. The extrapolated value of K_0

TABLE XI

BIMOLECULAR "CONSTANTS" FOR METHYLXANTHIC ACID AT 0°

v. Halban's table	$\sqrt{\mu}$	k	v. Halban's table	$\sqrt{\mu}$	k
16	0.0472	14.03	19	0.251	5.30
14	.0933	12.41	17	.359	3.05
15	.0933	11.89	20	.365	3.13
13	.135	8.95	25	.373	3.06
12	.143	9.61	17	.503	1.65
18	.182	7.47	21	.507	1.71
11	.190	7.54	26	.514	1.88
11	.193	6.40	17	.710	0.82
24	.200	7.10	22	.712	.91
10	.244	6.32	27	.717	.93

TABLE XII

$\sqrt{\mu}$	k_w/k	K
0.05	1.064	0.039
.1	1.230	.0435
.2	1.73	.055
.3	2.28	.070
.4	2.83	.087
.5	3.85	.106

The values of K above $\sqrt{\mu} = 0.2$ are actually too high, but are used in extrapolating to $\mu = 0$.

is 0.035, again in good agreement with the "average" of v. Halban. The broken lines again show the type of deviations from the theoretical to be expected for $\log k$ and $\log K$. We estimate that these values of K_0 cannot be in error by more than $\pm 5\%$.

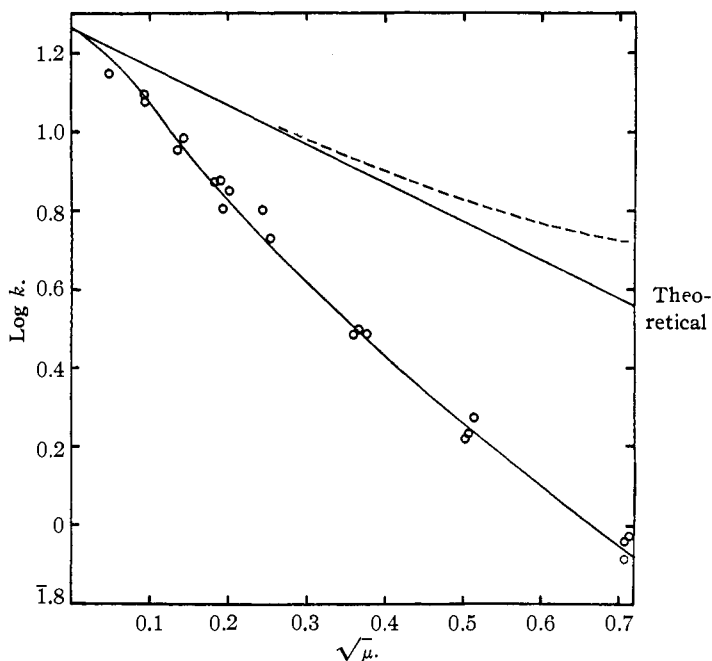


Fig. 3.—Comparison of the observed rates with the theoretical for methylxanthic acid at 0° : theoretical slope, -0.97 .

The Temperature Coefficient.—It is perhaps inaccurate to calculate the temperature coefficient from the data of v. Halban and Hecht at 0° and ours at 25° , since the rates were measured by different methods and at far different hydrogen-ion concentrations. However, the coefficient is certainly unusually high, as is to be expected from the rapidly decreasing stability of solutions of the acids and their salts as the temperature rises.

Using k_0 for ethylxanthic acid as 16.0 at 0° (Fig. 1) and 270 at 25°, we obtain an average coefficient per 10° rise of 6.75.

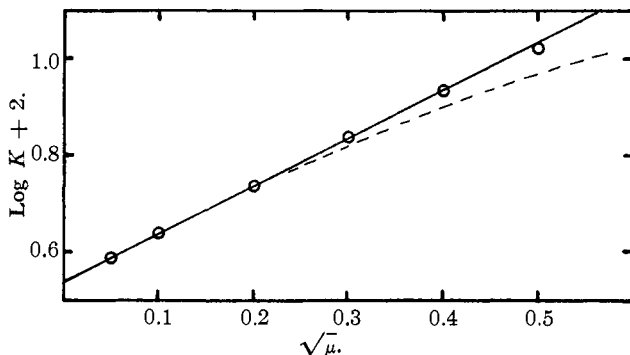


Fig. 4.—Variation in dissociation constant of methylxanthic acid with ionic strength (see Table XII): theoretical slope, +0.97.

Summary

Measurements of the rate of decomposition of ethylxanthic acid have been made at 25° in acetic acid–acetate and aniline–anilinium ion buffers and the primary and secondary salt effects analyzed.

Previous measurements of the rates for ethyl and methylxanthic acids have been analyzed and shown to be complicated by salt effects. The influence of salts on the dissociation constants of these acids has been shown.

The temperature coefficient of the rate has been calculated and shown to be unusually high.

NEW YORK CITY

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA, No. 91]

THE DISSOCIATION PRESSURE OF SILVER OXIDE BELOW 200°

BY ARTHUR F. BENTON AND LEONARD C. DRAKE

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Introduction

Le Chatelier¹ first showed that the reaction $\text{Ag}_2\text{O} = 2\text{Ag} + \frac{1}{2}\text{O}_2$ is reversible. Careful measurements of the equilibrium pressure were subsequently made by Lewis² over the temperature range 302–445°, and by Keyes and Hara³ from 374 to 500°. Close agreement was shown between the results of these two investigations.

Aside from the considerable interest which attaches to this system

¹ Le Chatelier, *Z. physik. Chem.*, **1**, 516 (1887).

² Lewis, *THIS JOURNAL*, **28**, 139 (1906).

³ Keyes and Hara, *ibid.*, **44**, 479 (1922).