

The Rate of Decarboxylation and the Dissociation Constants of Acetosuccinic Acid

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Solutions of acetosuccinic acid were prepared from the diethyl ester which was first hydrolysed in alkaline solution. In order to find the time required for practically complete hydrolysis, a few experiments on the rate of hydrolysis were carried out, but, owing to the complicated nature of the reaction, a complete kinetic analysis of the data was not attempted.

As a contribution to the study of the spontaneous decarboxylation of β -keto carboxylic acids in aqueous solution, a kinetic investigation was made of the decomposition of acetosuccinic acid into levulinic acid and carbon dioxide at the temperatures 25.0 and 37.0°C in solutions containing an excess of barium hydroxide (by titration), and in solutions of hydrochloric acid and in acetate buffer solutions (manometrically). By analysis of the data, separate rate constants were evaluated for each of the three simultaneous reactions: decarboxylation of undissociated acetosuccinic acid, of its univalent and divalent ion. It was found that acetate ions catalyse the decomposition of the undissociated acid. It was shown that cupric ions have only a small catalytic effect in the decarboxylation of acetosuccinic acid. In this respect the acid differs from other dibasic β -keto carboxylic acids, such as oxaloacetic acid, dihydroxytartaric acid, and acetonedicarboxylic acid, where cupric ions have a powerful catalytic effect.

The two dissociation constants of acetosuccinic acid at 25.0°C were determined by glass-electrode measurements on acetosuccinate buffer solutions containing various concentrations of sodium chloride. From the rate of change of the e.m.f. with time it was possible to compute rate constants for the decarboxylation which are in reasonable agreement with those obtained by manometry and by titration.

ALKALINE HYDROLYSIS OF DIETHYL ACETOSUCCINATE

The solutions of acetosuccinic acid examined in this paper were prepared from diethyl acetosuccinate which was hydrolysed in alkaline solution at room temperature or at 25°C shortly before the experiment was started. The ester was prepared as described in *Organic Syntheses*¹ and was distilled twice under reduced pressure through a Widmer stillhead in an all-glass apparatus. The purified preparation distilled within a temperature interval of 0.3°C.

Table 1. Hydrolysis of diethyl acetosuccinate at 25.0°C. Initial concentrations: x_0 M ester, u_0 M sodium hydroxide.

$x_0 = 0.03932$ $u_0 = 0.0899$			$x_0 = 0.03947$ $u_0 = 0.1198$			$x_0 = 0.04015$ $u_0 = 0.2099$		
t min	u	$k^* 10^2$	t min	u	$k^* 10^2$	t min	u	$k^* 10^2$
3.1	0.0808	1.72	4.0	0.1071	1.91	3.85	0.1941	2.52
7.9	0.0694	1.66	8.25	0.0961	1.88	7.9	0.1807	2.52
12.65	0.0601	1.64	12.2	0.0874	1.88	11.85	0.1700	2.54
17.45	0.0520	1.64	16.9	0.0788	1.89	16.1	0.1609	2.56
23.9	0.0436	1.62	22.5	0.0705	1.89	20.2	0.1541	2.56
30.0	0.0373	1.60	30.0	0.0619	1.92	25.1	0.1478	2.58
38.05	0.0310	1.58	40.0	0.0543	1.93	32.05	0.1411	2.64
48.1	0.0254	1.55	52.0	0.0485	1.95	39.5	0.1365	2.70
60.05	0.0208	1.52	65.0	0.0449	1.99	48.0	0.1332	2.81
			80.0	0.0426	2.08	60.05	0.1310	2.93

In order to get an idea of the time required for practically complete hydrolysis of the ester, a few rate-experiments were carried out at 25.0°C. The results are shown in Table 1 where the initial concentrations, x_0 M ester (Et_2X), u_0 M sodium hydroxide, are given at the top. At various times, t min after the ester was dissolved, samples were pipetted into a small excess of 0.05 M tartaric acid, and the mixture was quickly titrated back with sodium hydroxide. The concentrations of titratable base (u normal) found in the samples are given in the table. The reaction is kinetically rather complicated since it consists of two consecutive second- or first-order reactions, and, at large values of t , the slow decarboxylation of the acetosuccinate ion may affect the result. A complete kinetic analysis was therefore not attempted. Instead, $x = [\text{Et}_2\text{X}] + \frac{1}{2}[\text{EtX}^-]$ was computed by means of the equation $2x = u - (u_0 - 2x_0)$, and the equation for a first-order reaction, $k^* t = \log(x_0/x)$, was formally applied. Table 1 shows that k^* , within each of the three experiments, is roughly constant. In the first experiment k^* decreases a little, in the second it is almost constant until 90 %, in the third until 75 % of the ester is hydrolysed, after which it increases slowly. When the solutions examined in the following parts of this paper were prepared, the initial concentration of ester was in general about 0.04 M, and the concentration of base was about 0.12 N or more. It follows from Table 1 that the time of half life will here be less than 20 min at 25°C. In order to obtain practically complete hydrolysis, the solutions were therefore left for at least 4 h at 25°C or for at least 8 h at room temperature.

RATE OF DECARBOXYLATION IN BARIUM HYDROXIDE SOLUTIONS

When diethyl acetosuccinate is dissolved in an excess of strong base, the hydrolysis of the ester will be followed by a slow spontaneous decarboxylation of the divalent acetosuccinate ion

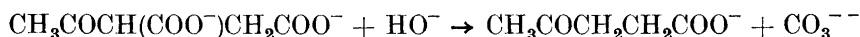


Table 2. Rate of decarboxylation of the divalent acetosuccinate ion by titration. Initial concentrations: x_0 M ester, u_0 N barium hydroxide.

Temperature 25.0°C $x_0 = 0.03903$, $u_0 = 0.1096$ $k = 0.191 \times 10^{-5} \text{ sec}^{-1}$				Temperature 37.0°C $x_0 = 0.03886$, $u_0 = 0.1093$ $k = 0.876 \times 10^{-5} \text{ sec}^{-1}$			
t hours	u	x	$x_0 e^{-kt}$	t hours	u	x	$x_0 e^{-kt}$
23.8	0.0255	0.0330	0.0331	4.50	0.0262	0.0335	0.0335
30.3	0.0241	0.0316	0.0314	6.33	0.0244	0.0317	0.0316
48.6	0.0205	0.0280	0.0280	8.00	0.0227	0.0300	0.0300
71.9	0.0163	0.0238	0.0238	12.33	0.0189	0.0262	0.0262
97.8	0.0127	0.0202	0.0200	24.50	0.0105	0.0178	0.0178
121.7	0.0095	0.0170	0.0169	28.50	0.0085	0.0158	0.0157
144.3	0.0071	0.0146	0.0145	31.25	0.0071	0.0144	0.0144
167.5	0.0049	0.0124	0.0124	48.83	0.0010	0.0083	0.0083
196.9	0.0025	0.0100	0.0101	48.92	0.0009	0.0082	0.0082
221.7	0.0006	0.0081	0.0086				

When the strong base is barium hydroxide, the carbonate ion will be precipitated as barium carbonate, and the rate of decarboxylation may be followed by taking samples of the solution, adding phenolphthalein, and titrating them with hydrochloric acid. Data for two experiments, at 25.0 and 37.0°C, respectively, are shown in Table 2. The initial concentrations, x_0 M ester and u_0 N barium hydroxide, are given at the top of the table. The concentration of acetosuccinate ion (x M) at the time t hours after the ester was dissolved, was calculated from the concentration of titratable base (u N) by means of the equation $x = 3x_0 - u_0 + u$. The reaction was found to obey the first-order law with the values of the rate constant k given at the top of the table. When k is expressed in reciprocal hours, and $x_0 e^{-kt}$ is computed, the values given in the last column of the two halves of the table are obtained. Comparison with the observed values of x shows that the agreement with the first-order formula is good. Table 3 gives a summary of all the experiments on the decomposition in barium hydroxide solution. It is seen that k decreases a little when salt is

Table 3. Rate of decarboxylation of the divalent acetosuccinate ion by titration.

Temperature °C	Initial concentrations in mole / liter				$k \times 10^5$ sec ⁻¹
	Ester	Ba(OH) ₂	BaCl ₂	KCl	
25.0	0.03903	0.0548	0	0	0.191
25.0	0.03876	0.0732	0	0	0.192
25.0	0.03902	0.1100	0	0	0.202
25.0	0.04067	0.0549	0.200	0	0.165
25.0	0.04082	0.0549	0	0.400	0.182
37.0	0.03886	0.0546	0	0	0.876
37.0	0.03917	0.1096	0	0	0.960

added. The decrease is larger for barium chloride than for potassium chloride. On the other hand, k increases with increasing hydroxyl ion concentration. This increase may possibly be due to an error caused by a simultaneous reaction



It is however known that this type of reaction, the so called acid decomposition of β -keto carboxylate ions, is predominant only in concentrated alkali. As the most probable values of the rate constant k_2 for the spontaneous decarboxylation of the divalent acetosuccinate ion we therefore adopt

$$\text{at } 25.0^\circ\text{C:} \quad k_2 = 0.191 \times 10^{-5} \text{ sec}^{-1}$$

$$\text{at } 37.0^\circ\text{C:} \quad k_2 = 0.876 \times 10^{-5} \text{ sec}^{-1}$$

When the Arrhenius equation is applied, the following expression is obtained

$$k_2 = 2.39 \times 10^{11} e^{-23300/RT} \text{ sec}^{-1}$$

DECOMPOSITION IN SOLUTIONS OF HYDROGEN CHLORIDE

Rate experiments were carried out at 25.0 and 37.0°C on solutions of hydrogen chloride and sodium chloride, the total chloride ion concentration being 0.300 M. The reaction was followed by observing the pressure above the solution in an apparatus described in an earlier paper². The difference P between the final pressure reading and the reading at the time t , is proportional to the total concentration (x M) of acetosuccinic acid at the time t : $P = \varphi x$, where φ is a constant. When α_0 , α_1 , and α_2 denote the fractions of the acid present in the form of undissociated acid (H_2X), univalent ion (HX^-), and divalent ion (X^{2-}), respectively, the rate of decarboxylation may be written as follows

$$-\frac{dx}{dt} = (k_0\alpha_0 + k_1\alpha_1 + k_2\alpha_2) x \quad (1)$$

where k_0 , k_1 , and k_2 are rate constants for the spontaneous decomposition of the molecules H_2X , HX^- , and X^{2-} , respectively. The expression in parenthesis will vary more or less during the reaction. At the end it will approach the value

$$k = k_0 \alpha_{0\infty} + k_1 \alpha_{1\infty} + k_2 \alpha_{2\infty} \quad (2)$$

where the subscript ∞ denotes final values of the variables, corresponding to a hydrogen ion concentration equal to the concentration of hydrogen chloride (h M).

In order to interpret the experiments, it was necessary to know the dissociation constants of acetosuccinic acid and levulinic acid. Those for acetosuccinic acid were determined in a later section of this paper where $K_1 = 1.56 \times 10^{-3}$ and $K_2 = 3.64 \times 10^{-5}$ were found for 0.300 M sodium chloride at 25°C. Owing to the instability of the acid, it was not possible to measure the constants at 37°. The values found for 25° were therefore applied also at 37°. Accascina³ has found the value 2.32×10^{-5} for the activity dissociation con-

stant of levulinic acid at 25°C. On the assumption that it increases with addition of sodium chloride in the same proportion as the dissociation constant of pyruvic acid⁴, the value 4.57×10^{-5} is estimated for the solvent 0.300 M sodium chloride.

We shall now deduce a formula by means of which we shall compute k for the decomposition in solutions containing hydrogen chloride. We may here neglect the second dissociation of acetosuccinic acid and the dissociation of levulinic acid. We therefore obtain from eqns. 1 and 2 and the expression for the first dissociation constant of acetosuccinic acid

$$-\frac{dx}{dt} = k_0x - (k_0 - k_1) \alpha_1 x \quad (3)$$

$$k = k_0 - (k_0 - k_1) \alpha_{1\infty} \quad (4)$$

$$\frac{\alpha_1 (h + \alpha_1 x)}{1 - \alpha_1} = \frac{\alpha_{1\infty} h}{1 - \alpha_{1\infty}} \quad (5)$$

By means of eqn. 5, x may be written as a function of $\alpha_1 x$

$$x = \frac{1}{\alpha_{1\infty}} (\alpha_1 x) + \frac{1 - \alpha_{1\infty}}{\alpha_{1\infty} h} (\alpha_1 x)^2 \quad (6)$$

When first eqn. 6 and then eqn. 4 are introduced into eqn. 3, is obtained

$$-\frac{1}{\alpha_{1\infty}} \frac{d(\alpha_1 x)}{dt} - \frac{2(1 - \alpha_{1\infty})}{\alpha_{1\infty} h} (\alpha_1 x) \frac{d(\alpha_1 x)}{dt} = \frac{k}{\alpha_{1\infty}} (\alpha_1 x) + \frac{k_0 (1 - \alpha_{1\infty})}{\alpha_{1\infty} h} (\alpha_1 x)^2$$

from which we get

$$-k dt = \frac{h d(\alpha_1 x) + 2(1 - \alpha_{1\infty}) (\alpha_1 x) d(\alpha_1 x)}{h (\alpha_1 x) + \frac{k_0}{k} (1 - \alpha_{1\infty}) (\alpha_1 x)^2}$$

which on integration gives

$$-kt + \text{const.} = \ln (\alpha_1 x) + \left(\frac{2k}{k_0} - 1 \right) \ln \left[h + \frac{k_0}{k} (1 - \alpha_{1\infty}) (\alpha_1 x) \right] \quad (7)$$

When eqn. 6 is solved with respect to $\alpha_1 x$ and the abbreviation

$$\lambda = 4 \alpha_{1\infty} (1 - \alpha_{1\infty}) / h \quad (8)$$

is used, we obtain

$$\alpha_1 x = \frac{h}{2(1 - \alpha_{1\infty})} (\sqrt{1 + \lambda x} - 1) = \frac{h \lambda x}{2(1 - \alpha_{1\infty})(1 + \sqrt{1 + \lambda x})} \quad (9)$$

If we further use the abbreviation

$$\varepsilon = 2(k_0 - k)/k_0 \quad (10)$$

and introduce eqn. 9 into eqn. 7, we get the formula

$$-kt + \text{const.} = \ln x - \ln(1 + \sqrt{1 + \lambda x}) + (1 - \varepsilon) \ln(1 - \varepsilon + \sqrt{1 + \lambda x}) \quad (11)$$

which may also be written in the form

$$-kt + \text{const.} = \ln x - \ln\left(1 + \frac{\sqrt{1 + \lambda x} - 1}{2}\right) + (1 - \varepsilon) \ln\left(1 + \frac{\sqrt{1 + \lambda x} - 1}{2 - \varepsilon}\right) \quad (12)$$

If we introduce $P = \varphi x$, write λ' instead of λ/φ , and transform to decadic logarithms, we get

$$\begin{aligned} -0.4343 kt + \text{const.} = \log P - \log\left(1 + \frac{\sqrt{1 + \lambda' P} - 1}{2}\right) + (1 - \varepsilon) \\ \log\left(1 + \frac{\sqrt{1 + \lambda' P} - 1}{2 - \varepsilon}\right) \end{aligned} \quad (13)$$

When the hydrogen ion concentration is sufficiently large, λ will be so small that formula 13 may be simplified (using $\ln(1 + \delta) \simeq \delta$, and $\sqrt{1 + \delta} - 1 \simeq \delta/2$) to

$$-0.4343 kt + \text{const.} = \log P - \frac{0.4343 \varepsilon \lambda'}{4(2 - \varepsilon)} P \quad (14)$$

If further $k_1 \alpha_{1\infty} \ll k_0(1 - \alpha_{1\infty})$ we find by means of eqns. 4 and 10 that $\varepsilon \simeq 2\alpha_{1\infty}$ which on introduction into eqn. 14 gives the following approximate formula in which k does not appear on the right side of the equation

$$-0.4343 kt + \text{const.} = \log P - \frac{0.4343 \alpha_{1\infty}^2}{\varphi h} P \quad (15)$$

The composition of the solutions examined and the results obtained are given in Table 4. The initial concentrations of acetosuccinic acid (x_0 M), given in the third column, have been calculated on the assumption that the ester has been completely hydrolysed while none of the acetosuccinic acid has been decarboxylated. Actually, up to 20 % of the acid had been decomposed when readings began, partly in alkaline solution and partly after the addition of hydrochloric acid, but this, of course, does not affect the kinetic result. The ethanol ($2x_0$ M) present in the solutions was produced by the hydrolysis. The degrees of dissociation $\alpha_{1\infty}$ and $\alpha_{2\infty}$ were calculated by means of the dissociation constants given before. In computing the rate constants k , it was for most of the solutions accurate enough to apply formula 15. For the other solutions, the approximate value of k found by means of this formula was used for the calculation of ε by means of eqn. 10 after which the exact formula 13 was applied. When the values of the expression on the right side of the equation were plotted against t , the points fell always very close to a straight line from the slope of which the final value of k was determined.

The reaction is, in the solutions examined here, predominantly a spontaneous decarboxylation of the undissociated acid. The data were therefore used for calculating k_0 by means of eqn. 2. It follows from the values of k_2

Table 4. Decarboxylation of acetosuccinic acid (initially x_0 M) in the solvent: h M hydrogen chloride, c M cupric nitrate, $(0.300-h-3c)$ M sodium chloride, $2x_0$ M ethanol.

h	c	x_0	$\alpha_{1\infty}$	$\alpha_{2\infty}$	$k \times 10^5$ sec ⁻¹	$k_0 \times 10^5$ sec ⁻¹
<i>Temperature 25.0°C:</i>						
0.2700	0	0.0100	0.0057	0.0000	17.18	17.26
0.2400	0	0.0196	0.0065	0.0000	17.19	17.28
0.0900	0	0.0207	0.0170	0.0000	17.08	17.32
0.0900	0.00400	0.0208	0.0170	0.0000	17.02	17.26
0.0400	0	0.0194	0.0375	0.0000	16.71	17.24
0.0200	0	0.0199	0.0723	0.0001	16.11	17.13
0.01494	0	0.0103	0.0948	0.0002	15.86	17.20
0.01200	0	0.0197	0.1150	0.0004	15.64	17.28
0.01200	0.00400	0.0200	0.1150	0.0004	15.57	17.20
0.00591	0	0.0101	0.2086	0.0013	14.15	17.10
0.00293	0	0.0106	0.3460	0.0042	12.30	17.30
<i>Temperature 37.0°C:</i>						
0.2400	0	0.0200	0.0065	0.0000	73.8	74.1
0.0900	0	0.0201	0.0170	0.0000	72.8	73.8
0.0400	0	0.0205	0.0375	0.0000	71.7	73.9
0.01980	0	0.0200	0.0730	0.0002	70.4	74.7
0.01946	0	0.0198	0.0741	0.0002	70.5	75.0
0.01190	0	0.0206	0.1159	0.0004	68.3	75.1

found in the preceding part of the paper that the last term of the equation may be neglected. When k_1 found in experiments on acetate buffers in the next part of the paper is applied, k_0 given in the last column of Table 4 is computed. The average values at the two temperatures are

$$\text{at } 25.0^\circ\text{C:} \quad k_0 = 17.23 \times 10^{-5} \text{ sec}^{-1}$$

$$\text{at } 37.0^\circ\text{C:} \quad k_0 = 74.3 \times 10^{-5} \text{ sec}^{-1}$$

When the Arrhenius equation is applied, the following expression is obtained

$$k_0 = 4.38 \times 10^{12} e^{-22400/RT} \text{ sec}^{-1}$$

Two of the solutions in Table 4 contained cupric nitrate while the total ionic strength was the same as in the other solutions. The results show that cupric ions have no catalytic effect.

DECOMPOSITION IN ACETATE BUFFER SOLUTIONS

The rate of decarboxylation was studied by the manometric method at 25.0 and 37.0°C in solutions containing acetic acid, sodium acetate, and, in some cases, sodium chloride, the total ionic strength being always close to 0.300. The composition of the solutions examined is shown in Table 5.

In applying eqn. 1 to the experimental data, it must be taken into account that α_0 , α_1 , and α_2 change a little as the reaction progresses, from their initial values α_{00} , α_{10} , and α_{20} (corresponding to the presence of x_0 M acetosuccinic

acid) to their final values $\alpha_{0\infty}$, $\alpha_{1\infty}$, and $\alpha_{2\infty}$ (when practically all acetosuccinic acid has been transformed into levulinic acid and carbon dioxide). In order to correct for this change, it was as an approximation assumed that α_0 , α_1 , and α_2 vary linearly with x . Eqn. 1 may then be written as

$$-\frac{dx}{dt} = (k + \beta x)x \quad (16)$$

where we have used the abbreviation

$$\beta = [k_0 (\alpha_{00} - \alpha_{0\infty}) + k_1 (\alpha_{10} - \alpha_{1\infty}) + k_2 (\alpha_{20} - \alpha_{2\infty})] / x_0 \quad (17)$$

By integration of eqn. 16, transformation to decadic logarithms, and insertion of $P = \varphi x$ and $\beta' = \beta/\varphi$, is obtained

$$-0.4343 kt + \text{const.} = \log P - \log (1 + \beta' P) \quad (18)$$

The initial and final values of α_0 , α_1 , and α_2 were computed for all the solutions examined. In this computation were used the values of the dissociation constants of acetosuccinic acid and levulinic acid given in the preceding section of the paper. For the dissociation constant of acetic acid was, both at 25 and 37°C, used the value 3.20×10^{-5} estimated for the solvent 0.3 M sodium chloride on the basis of measurements by Harned and Hickey⁵ and by Kilpatrick and Eanes⁶. The slight dissociation of carbonic acid was neglected. In Table 5 are, to save space, given only $\alpha_{0\infty}$ and $\alpha_{1\infty}$ together with the final acetate ion concentration $[\text{Ac}^-]_{\infty}$.

Table 5. Decarboxylation of acetosuccinic acid (initially x_0 M) in the solvent: a M acetic acid, b M sodium acetate, $(0.300 - b)$ M sodium chloride, $2x_0$ M ethanol.

a	b	x_0	$[\text{Ac}^-]_{\infty}$	$\alpha_{0\infty}$	$\alpha_{1\infty}$	$k \times 10^5$ sec ⁻¹	$k \times 10^5$ sec ⁻¹ calc.
<i>Temperature 25.0°C:</i>							
0.4923	0.3000	0.01146	0.2948	0.0203	0.587	2.503	2.504
0.3182	0.3001	0.01156	0.2936	0.0111	0.490	1.936	1.938
0.1797	0.3000	0.01147	0.2921	0.0048	0.361	1.369	1.374
0.1091	0.3000	0.01157	0.2910	0.0022	0.264	1.011	1.015
0.4923	0.1500	0.01169	0.1466	0.0494	0.713	3.423	3.418
0.3182	0.1501	0.01146	0.1456	0.0292	0.644	2.736	2.734
0.1797	0.1500	0.01145	0.1441	0.0139	0.526	2.033	2.029
0.1091	0.1501	0.01167	0.1427	0.0070	0.417	1.559	1.552
<i>Temperature 37.0°C:</i>							
0.4920	0.3000	0.01095	0.2950	0.0203	0.587	12.48	12.45
0.2836	0.3000	0.01118	0.2933	0.0094	0.463	9.14	9.20
0.1786	0.3000	0.01112	0.2924	0.0047	0.359	7.05	7.02
0.1088	0.3000	0.01140	0.2911	0.0022	0.263	5.25	5.22
0.4920	0.1500	0.01134	0.1468	0.0493	0.712	16.81	16.74
0.3876	0.1501	0.01137	0.1462	0.0372	0.677	15.00	15.01
0.2832	0.1501	0.01127	0.1454	0.0252	0.621	12.92	12.95
0.1786	0.1500	0.01125	0.1445	0.0137	0.523	10.13	10.32
0.1088	0.1500	0.01123	0.1429	0.0069	0.415	8.06	7.98

When k was computed from the observed data by means of eqn. 18, a method of successive approximations had to be used, since β' was unknown at the start. In the final step, when β' was calculated from eqn. 17 by means of the constants in the expressions for k given below (eqns. 19 and 20), the values of k shown in the next to the last column of Table 5 were obtained. When eqn. 2 was applied, it was found that k_0 could not have the value found previously for solutions of hydrogen chloride. Agreement could, however, be obtained when it was assumed that k_0 increases linearly with the acetate ion concentration, that is, acetate ions catalyse the decarboxylation of undissociated acetosuccinic acid. On this basis the following expressions for the rate constants were obtained

$$25.0^\circ: k \times 10^5 = (17.23 + 47.8 [\text{Ac}^-])\alpha_{0\infty} + 3.054 \alpha_{1\infty} + 0.191 \alpha_{2\infty} \quad (19)$$

$$37.0^\circ: k \times 10^5 = (74.3 + 166 [\text{Ac}^-])\alpha_{0\infty} + 16.37 \alpha_{1\infty} + 0.876 \alpha_{2\infty} \quad (20)$$

Each of the expressions contains two new constants, k_1 and the catalytic coefficient of the acetate ion (k_{Ac^-}), which have been computed so as to obtain the best agreement with the observed values of k . The last column of Table 5 shows k calculated by means of eqns. 19 and 20. When the Arrhenius equation is applied, the following expressions are obtained

$$k_1 = 2.10 \times 10^{14} e^{-25700/RT} \text{ sec}^{-1}$$

and $k_{\text{Ac}^-} = 4.54 \times 10^{10} e^{-19100/RT} \text{ liter mole}^{-1} \text{ sec}^{-1}$

Cupric ion catalysis. In Table 6 are given the results of rate measurements on acetate buffer solutions containing 0.00480 M cupric nitrate, the total ionic

Table 6. Decarboxylation of acetosuccinic acid (initially x_0 M) in the solvent: a M acetic acid, b M sodium acetate, 0.00480 M cupric nitrate, $(0.236 - b)$ M sodium chloride, $2x_0$ M ethanol.

a	b	x_0	$[\text{Ac}^-]_{\infty}$	$[\text{Cu}^{++}]_{\infty}$ $\times 10^3$	$\alpha_{0\infty}$	$\alpha_{1\infty}$	$k \times 10^5$ sec^{-1}	$k \times 10^5$ sec^{-1} calc.
<i>Temperature 25.0°C:</i>								
0.3029	0.2856	0.01101	0.2719	0.151	0.0116	0.496	2.026	1.960
0.1711	0.2856	0.01101	0.2705	0.152	0.0050	0.367	1.481	1.392
0.1039	0.2856	0.01102	0.2695	0.153	0.0023	0.269	1.140	1.031
0.4687	0.1428	0.01113	0.1334	0.429	0.0522	0.719	3.513	3.471
0.3029	0.1428	0.01091	0.1324	0.433	0.0310	0.652	2.824	2.782
0.1711	0.1428	0.01090	0.1309	0.440	0.0149	0.537	2.173	2.075
0.1039	0.1428	0.01111	0.1296	0.445	0.0075	0.428	1.729	1.591
<i>Temperature 37.0°C:</i>								
0.4684	0.2855	0.01084	0.2731	0.150	0.0211	0.593	12.87	12.57
0.2700	0.2855	0.01074	0.2718	0.151	0.0098	0.469	9.64	9.31
0.1700	0.2856	0.01095	0.2705	0.153	0.0049	0.366	7.64	7.13
0.1036	0.2856	0.01068	0.2697	0.153	0.0023	0.268	6.03	5.30
0.1700	0.1429	0.01070	0.1311	0.439	0.0147	0.535	10.94	10.57
0.1036	0.1429	0.01099	0.1297	0.445	0.0075	0.427	8.93	8.21

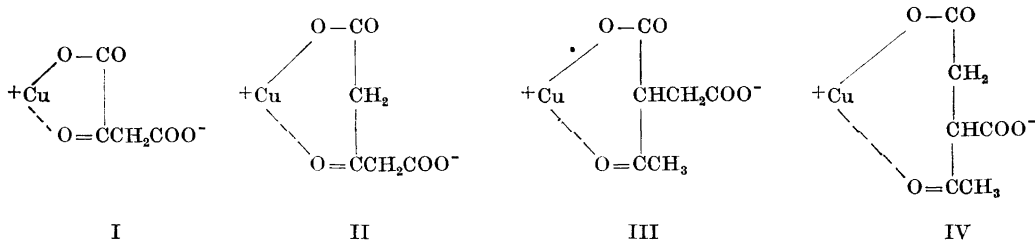
strength being 0.300. It was here necessary to take into account the complex formation between cupric and acetate ions while that between cupric and chloride ions was neglected. The initial and final values of the acetate, cupric, and hydrogen ion concentrations, and of α_0 , α_1 , and α_2 , were computed by means of the dissociation constants of the acids given before and the following values of the complexity constants⁷, corresponding to the ionic strength 0.300

$$[\text{CuAc}^+] / [\text{Cu}^{++}] [\text{Ac}^-] = 41.2$$

$$[\text{CuAc}_2] / [\text{Cu}^{++}] [\text{Ac}^-]^2 = 264$$

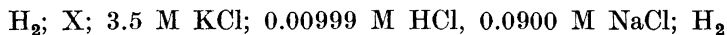
Only the final values of the acetate and cupric ion concentrations, and of α_0 and α_1 , are given in Table 6. Rate constants k , computed from the observed data by the same procedure as for solutions without cupric nitrate, are given in the next to the last column. They are from 1 to 14 % higher than those shown in the last column which were computed by means of eqns. 19 and 20 on the assumption that cupric ions do not catalyse. The difference indicates that cupric ions have a small catalytic effect in the decarboxylation of acetosuccinic acid. The data are not accurate enough to establish a mechanism for the catalytic reaction, but they agree best with the assumption that the rate is proportional to the product $[\text{CuAc}^+] \alpha_2$.

It has been found earlier that certain metal ions, especially cupric ions, have a powerful catalytic effect in the decarboxylation of other dibasic β -keto carboxylic acids, such as oxaloacetic acid^{8,9}, dimethyloxaloacetic acid¹⁰, acetonedicarboxylic acid¹¹, and dihydroxytartaric acid¹². This catalysis was explained as being the result of a rapid decarboxylation of a complex of the chelate type between the metal ion and the divalent β -keto carboxylate ion. In this complex, the metal ion is bound to a keto and a carboxylate group. It is essential that a carboxylate group having a keto group in β -position is free, since a metal ion seems to stabilise the carboxylate group to which it is bound. Thus, the metal ion complexes of the nitroacetate ion do not split off carbon dioxide¹³. The chelates which decompose rapidly would therefore in oxaloacetic acid have the five-membered ring structure I, and in acetonedicarboxylic acid the six-membered ring structure II. In acetosuccinic acid two chelates are conceivable, the six-membered ring structure III and the seven-membered ring structure IV. The former would not be expected to split off carbon dioxide, and the latter may possibly be formed less readily since it has a seven-membered ring.



THE DISSOCIATION CONSTANTS OF ACETOSUCCINIC ACID

The first and second dissociation constant of acetosuccinic acid were determined by glass-electrode measurements at 25.0°C on acetosuccinate buffer solutions containing various concentrations of sodium chloride. The measurements were carried out, and the hydrogen ion concentrations computed, by the procedure followed by the author in earlier papers ^{4,14}. By the measurements was determined what is actually the e.m.f. (E volts) of cells of the composition



where X is the acetosuccinate buffer under investigation.

The buffer solutions were prepared in the following way. Diethyl acetosuccinate was weighed out and dissolved in a solution of sodium hydroxide and sodium chloride (concentrations shown in Table 10). The mixture was placed in a thermostat at 25.0°C. According to measurements in the first part of this paper, the ester was completely hydrolysed within 4 h. The buffer solutions to be measured were prepared by adding appropriate volumes of hydrochloric acid and water to samples taken from the alkaline solution after complete hydrolysis. If no decarboxylation had taken place, the solutions would have the composition shown in Tables 7 and 8 (x_0 M acetosuccinic acid, b M sodium hydroxide, s M sodium chloride, $2x_0$ M ethanol). Actually, more or less of the acetosuccinic acid had been transformed into levulinic acid and carbon dioxide when the measurement took place, partly by a slow reaction in alkaline solution, and partly by a more rapid reaction after acidification. In order to find the hydrogen ion concentration of solutions where no decarboxylation had taken place, two extrapolations were made, one to correct for decarboxylation in acid solution and another to correct for decarboxylation in the alkaline solution from which the buffer was made. In order to make the first extrapolation, E was measured with an interval of one minute in the time from 4 or 5 to 25 or 30 min after the acidification. When E was plotted against the time (t minutes after acidification of the solution), the points fell close to a straight line by means of which E corresponding to $t = 0$ was found. Three or four such series of measurements were carried out on buffer solutions of the same composition except that they were made up from the alkaline solution at different times (τ hours after its preparation). E corresponding to $t = 0$ for each series was plotted against τ , and E_0 was found by extrapolation to $\tau = 0$. In evaluating τ , a small correction was subtracted (estimated to be 0.4 h) in order to allow for the space of time in which the ester was not completely hydrolysed. Values of $-\log[\text{H}^+]_0$, pertaining to solutions where no decarboxylation had taken place, were calculated from E_0 . They are given in Tables 7 and 8 together with, respectively, $-\log K_1$ and $-\log K_2$ computed from them in the usual way. In the tables are also shown the ionic strengths I of the solutions. When Debye-Hückel's limiting law is applied, it is found that the results may be expressed by the formulae

$$-\log K_1 = 3.048 - 1.013 \sqrt{I} / (1 + 2.38 \sqrt{I}) \quad (21)$$

$$-\log K_2 = 4.952 - 2.026 \sqrt{I} / (1 + 2.12 \sqrt{I}) \quad (22)$$

Table 7. First dissociation constant (K_1) of acetosuccinic acid at 25.0°C.

	$x_0 \times 10^3$	$b \times 10^3$	s	I	$-\log [H^+]_0$	$-\log K_1$	$-\log K_1$ calc.
A1	9.99	3.90	0.2959	0.3014	2.836	2.805	2.807
A2	10.00	4.92	0.2948	0.3010	2.493	2.802	2.807
A3	10.03	5.78	0.2939	0.3009	3.047	2.814	2.807
A4	10.03	3.89	0.1959	0.2013	2.853	2.835	2.828
A5	10.02	4.92	0.1949	0.2011	2.956	2.820	2.828
A6	10.04	5.80	0.1941	0.2010	3.065	2.831	2.828
A7	10.02	3.90	0.0960	0.1013	2.876	2.865	2.865
A8	10.01	4.92	0.0949	0.1010	2.994	2.870	2.865
A9	10.02	5.78	0.0941	0.1009	3.089	2.857	2.865

When $-\log K_1$ and $-\log K_2$ are calculated by means of these expressions, the values given in the last column of Tables 7 and 8 are obtained. If it is permissible to extrapolate to $I = 0$ by means of eqns. 21 and 22, the two activity dissociation constants are $K_1 = 8.95 \times 10^{-4}$ and $K_2 = 1.12 \times 10^{-5}$.

For the buffer solutions examined in the first three lines of Table 7 (A 1—3) and the first three lines of Table 8 (B 1—3) are in Table 9 given the values of E and $-\log[H^+]$ found by extrapolation of the observed data to the time ($t = 0$) when the solution was acidified. In order to show how rapidly E changes, values of E and $-\log [H^+]$ corresponding to either $t = 10$ or $t = 20$ min are also given for most of the solutions. All the solutions of Table 9 were prepared from alkaline solutions of the same initial composition (given in the first line of Table 10).

Rate of decarboxylation from e.m.f. measurements. In order to estimate the rate of decarboxylation both in the alkaline solutions and in the buffer solutions, the concentrations of undecomposed acetosuccinic acid (x molar) were calculated from the hydrogen ion concentrations by means of the following formula (expressing the principle of electroneutrality)

$$(\alpha_1 + 2\alpha_2) x + (\alpha' + \alpha'') (x_0 - x) = b + [H^+] \quad (23)$$

Table 8. Second dissociation constant (K_2) of acetosuccinic acid at 25.0°C.

	$x_0 \times 10^3$	$b \times 10^3$	s	I	$-\log [H^+]_0$	$-\log K_2$	$-\log K_2$ calc.
B1	9.99	13.89	0.2858	0.3039	4.299	4.436	4.437
B2	10.00	14.91	0.2848	0.3048	4.460	4.441	4.437
B3	10.03	15.89	0.2838	0.3057	4.603	4.433	4.436
B4	10.03	13.88	0.1859	0.2039	4.337	4.489	4.484
B5	10.02	14.90	0.1848	0.2048	4.502	4.491	4.484
B6	10.04	15.90	0.1840	0.2059	4.638	4.468	4.483
B7	10.02	13.89	0.0860	0.1040	4.419	4.574	4.564
B8	10.01	14.90	0.0849	0.1048	4.577	4.566	4.563
B9	10.02	15.89	0.0840	0.1058	4.719	4.550	4.562

Table 9. Glass-electrode measurements at 25.0°C on acetosuccinate buffer solutions.

	τ hours	t min	E	$-\log$ [H ⁺]	$x \times 10^3$	$k_2 \times 10^5$ sec ⁻¹	$k \times 10^5$ sec ⁻¹	$k \times 10^5$ sec ⁻¹ calc.
A1	5.3	0	0.0498	2.854	9.67	0.171	9.4	9.5
		10	0.0516	2.884	9.14			
	24.4	0	0.05345	2.915	8.65	0.164	9.1	9.0
		10	0.0553	2.946	8.19			
	30.6	0	0.0547	2.938	8.31	0.167	8.7	8.8
		10	0.0565	2.969	7.88			
A2	4.7	0	0.0563	2.963	9.73	0.162	8.4	8.6
		10	0.0583	2.997	9.25			
	22.9	0	0.06095	3.042	8.65	0.176	7.9	7.9
		10	0.06295	3.076	8.25			
	48.0	0	0.06725	3.149	7.48	0.168	7.3	7.1
		10	0.06925	3.183	7.16			
A3	5.2	0	0.0629	3.074	9.63	0.217	7.6	7.7
		10	0.06495	3.109	9.20			
	10.2	0	0.0645	3.101	9.30	0.206	7.4	7.5
		10	0.0666	3.137	8.89			
	28.5	0	0.0694	3.184	8.40	0.173	6.9	6.8
		10	0.0715	3.220	8.06			
B1	5.8	0	0.13795	4.343	9.68	0.151	2.3	2.0
		20	0.1401	4.379	9.42			
	23.7	0	0.1461	4.481	8.70	0.162	1.7	1.7
		20	0.1477	4.508	8.52			
	29.9	0	0.14835	4.519	8.44	0.157	2.1	1.6
		20	0.1502	4.550	8.23			
	48.9	0	0.1563	4.653	7.54	0.160	1.8	1.3
		20	0.1578	4.678	7.38			
B2	5.2	0	0.14735	4.502	9.68	0.173		
	23.4	0	0.1559	4.647	8.70	0.166		
	29.1	0	0.15865	4.693	8.41	0.165		
	48.8	0	0.1673	4.839	7.53	0.161		
B3	5.8	0	0.1564	4.653	9.72	0.150		
	10.7	0	0.1591	4.698	9.44	0.157		
	25.5	0	0.16655	4.824	8.69	0.156		
	28.9	0	0.16845	4.856	8.50	0.159		

Table 10. Rate of decarboxylation in alkaline solution at 25.0°C from glass-electrode measurements.

Solutions	Ester mole/liter	NaOH mole/liter	NaCl mole/liter	$k_2 \times 10^5$ sec ⁻¹ (A)	$k_2 \times 10^5$ sec ⁻¹ (B)
A 1-3, B 1-3	0.0400	0.0995	1.100	0.173	0.160
A 4-6, B 4-6	0.0400	0.0995	0.700	0.177	0.166
A 7-9, B 7-9	0.0400	0.0995	0.300	0.188	0.174

While α_1 and α_2 have the same meaning as earlier in this paper, α' is the fraction of levulinic acid present as ion, and α'' is the fraction of carbon dioxide present as univalent ion (may be neglected for the solutions A 1-9). The values of α_0 , α_1 , and α_2 were computed from $[H^+]$ by means of the dissociation constants calculated from eqns. 21 and 22. In the computation of α' were used the following values of the dissociation constant of levulinic acid: 3.95×10^{-5} , 4.42×10^{-5} , and 4.57×10^{-5} , at the ionic strengths 0.1, 0.2, and 0.3, respectively (estimated from the measurements of Accascina³ as explained earlier). The values of the dissociation constant of carbonic acid used in calculating α'' , 7.8×10^{-7} , 9.0×10^{-7} , and 9.8×10^{-7} , at the ionic strengths 0.1, 0.2, and 0.3, respectively, were taken from a paper by Näsänen¹⁵.

Values of x calculated by means of eqn. 23 are given in the sixth column of Table 9. In the next column are given the rate constants k_2 for the decarboxylation in alkaline solution computed by means of the formula for a first-order reaction from the values of x corresponding to $t = 0$ and x_0 given in Tables 7 and 8. The average value of k_2 for the series A 1-3 is 0.173×10^{-5} sec⁻¹, while for the series B 1-3 it is a little lower, 0.160×10^{-5} sec⁻¹. The results of similar calculations for the other solutions examined are summarised in Table 10. It is seen that the B-series always give a lower value than the A-series. A comparison with the values of k in Table 3 will show that there is a reasonable agreement between the values obtained by the titration method and those found by means of glass-electrode measurements.

The rate constants k for the decarboxylation in the buffer solutions given in the next to the last column of Table 9 were computed by means of the first-order formula from the two values of x shown in the table for each solution. Since the fractions α_0 , α_1 , and α_2 change a little in the interval examined, the reaction will not follow the first-order law strictly, but the values of k obtained should hold approximately for a solution in which α_0 , α_1 , and α_2 are constant and equal to the average of their values at the beginning and end of the interval. If k is calculated from the average values by means of formula 19 ($[Ac^-] = 0$), the values shown in the last column of Table 9 are obtained. They are in reasonable agreement with those found from the electrometric measurements.

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