

The Hydrolysis of Ethyl Acetoacetate and the Decarboxylation of Acetoacetic Acid in Strongly Acid Solution

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The first-order rate constants for the hydrolysis of ethyl acetoacetate and for the decarboxylation of acetoacetic acid, k_1 and k_2 , respectively, have been measured at 37°C in concentrated solutions of hydrochloric, sulphuric, and perchloric acid (in some cases added sodium or potassium salt of the strong acids). The rate constants were computed from the observed rate of production of carbon dioxide, in solutions of the ester and solutions of the free keto-acid, respectively. It was found that k_2 decreased linearly with increasing concentration of strong acid or salt, while $\log(k_1/[H^+])$ was found to increase linearly with increasing concentration of hydrochloric or sulphuric acid, but pass through a minimum in solutions of perchloric acid.

When a β -keto carboxylic ester is dissolved in an aqueous solution of a strong acid two consecutive first-order reactions, acid hydrolysis of the ester (rate constant k_1) and decarboxylation of the free keto-acid (rate constant k_2), will occur. If k_1 is not much larger than k_2 , and if k_2 is known from separate experiments, it is possible to calculate k_1 from the observed rate of production of carbon dioxide. Since our knowledge of the rate of ester hydrolysis in strongly acid medium is rather scanty, it was found worth while to apply this method to the study of the hydrolysis of ethyl acetoacetate in concentrated solutions of hydrochloric, sulphuric, and perchloric acid.

The ethyl acetoacetate used for the measurements was an old preparation which had been carefully purified through the sodium hydrogen sulphite compound and by distillation¹. The other substances were commercial *pro analysi* preparations. Experiments were carried out at the temperature 37.0°C by means of an apparatus described earlier². The production of carbon dioxide was followed by observing the pressure above the solution.

RATE OF DECARBOXYLATION OF ACETOACETIC ACID

Solutions of free acetoacetic acid were prepared in the following way. Ethyl acetoacetate was dissolved in about 4/3 of the amount of sodium hydroxide solution necessary for hydrolysis. The mixture was left at room temperature

Table 1. Decarboxylation of acetoacetic acid at 37.0°C in solutions of hydrochloric acid.

[HCl]	[NaCl]	$k \times 10^5$	$k_2 \times 10^5$ calc.	[HCl]	[NaCl]	[KCl]	$k_2 \times 10^5$	$k_2 \times 10^5$ calc.
0.23	0.02	8.07	8.11	0.51	2.02		6.74	6.81
0.50	0.02	8.00	8.00	0.51	3.02		6.14	6.22
0.98	0.02	7.81	7.80	0.51	4.02		5.69	5.63
1.98	0.02	7.38	7.38	0.98	1.02		7.21	7.21
2.99	0.02	6.98	6.95	0.98	2.02		6.61	6.62
4.01	0.02	6.54	6.52	0.51	0.02	1.00	7.68	7.66
4.51	0.02	6.29	6.31	0.51	0.02	2.00	7.31	7.33
0.51	1.02	7.45	7.40	0.51	0.02	3.00	7.02	7.00

Table 2. Decarboxylation of acetoacetic acid at 37.0°C in solutions of sulphuric acid.

[H ₂ SO ₄]	[NaHSO ₄]	$k_2 \times 10^5$	$k_2 \times 10^5$ calc.
0.23	0.02	8.13	8.20
0.48	0.02	8.04	8.01
0.98	0.02	7.64	7.62
1.99	0.02	6.87	6.84
2.99	0.02	6.06	6.06
4.00	0.02	5.29	5.28
5.00	0.02	4.43	4.50
6.01	0.02	3.74	3.72
6.97	0.02	2.97	2.97
7.95	0.02	2.27	2.21
10.02	0.02	1.16	0.60

Table 3. Decarboxylation of acetoacetic acid at 37.0°C in solutions of perchloric acid.

[HClO ₄]	[NaClO ₄]	$k_2 \times 10^5$	$k_2 \times 10^5$ calc.
0.08	0.02	8.14	8.40
0.48	0.02	7.97	8.04
0.98	0.02	7.60	7.59
1.98	0.02	6.70	6.70
2.98	0.02	5.80	5.80
3.98	0.02	4.94	4.91
4.98	0.02	4.00	4.01
5.98	0.02	3.12	3.12
0.98	1.02	6.46	6.55
0.98	2.02	5.60	5.51

for at least 16 h after which time hydrolysis was complete. Appropriate amounts of this solution, the strong acid, and, in some experiments, salt solution were pipetted into the reaction vessel. The initial concentration of acetoacetic acid was in all the kinetic experiments about 0.015 M. The solutions contained in addition about 0.015 M ethanol produced by hydrolysis of the ester, and about 0.020 M sodium salt of the strong acid produced by neutralisation of the sodium hydroxide used for the hydrolysis. The reaction was always found to follow the first-order law. In Tables 1, 2, and 3 are given the molar concentrations of the solutions examined and the rate constants k_2 found (in sec⁻¹). The values of k_2 decrease nearly linearly with increasing concentration of strong acid or salt, and may be expressed by the formulae

$$k_2 \times 10^5 = 8.22 - 0.42[\text{HCl}] - 0.59[\text{NaCl}] - 0.33[\text{KCl}] \quad (1)$$

$$k_2 \times 10^5 = 8.38 - 0.776[\text{H}_2\text{SO}_4] \quad (2)$$

$$k_2 \times 10^5 = 8.49 - 0.895[\text{HClO}_4] - 1.04[\text{NaClO}_4] \quad (3)$$

Values of k_2 calculated from these expressions are given in the last column of the three tables. The agreement is good except for 8 and 10 M H_2SO_4 and for small concentrations of the acids where the experimental values are smaller than those calculated from the formulae (most pronounced for 0.08 M HClO_4). This discrepancy is not due to dissociation of the acetoacetic acid since its dissociation constant³ is as small as 3×10^{-4} . The failure of the formulae at small concentrations is also apparent from the fact that for zero concentration of strong acid and salt they give different values of k_2 . The effect of strong acids on k_2 therefore seems to be composed of two parts, a moderate increase which reaches its full value in less than 1 M solution, and the predominating linear decrease. It follows from the formulae 1–3 that there is a close similarity between the effects of the strong acids and the salts; both are salt effects.

RATE OF HYDROLYSIS OF ETHYL ACETOACETATE

The ester was weighed out in a small platinum bucket which was suspended in the apparatus above the solution of strong acid in such a way that it could be released when the apparatus had been evacuated and pressure and temperature equilibrium was attained. Pressure readings were taken from the moment when the ester was dissolved. The difference P between the final pressure reading and the reading at the time t is proportional to the sum x of the concentrations of keto-ester and free keto-acid. The rate constants for the hydrolysis and the decarboxylation, k_1 and k_2 , respectively, were in most cases of the same order of magnitude. Therefore, the following formula, known from text-books on chemical kinetics, was applied (x_0 denotes the initial ester concentration)

$$x = x_0 \left(\frac{k_1}{k_1 - k_2} e^{-k_2 t} - \frac{k_2}{k_1 - k_2} e^{-k_1 t} \right)$$

By rearrangement is obtained

$$(x - x_0 e^{-k_2 t})/k_2 = (x - x_0 e^{-k_1 t})/k_1 = x_0 e^{-k_2 t} (1 - e^{-(k_1 - k_2)t}) / (k_1 - k_2)$$

$$(k_1 - k_2) t / (1 - e^{-(k_1 - k_2)t}) = k_2 t e^{-k_2 t} / \left(\frac{x}{x_0} - e^{-k_2 t} \right)$$

When we remember that P is proportional to x and set

$$0.4343 k_1 = k_1^*, \quad 0.4343 k_2 = k_2^*$$

$$(k_1^* - k_2^*) t = y \tag{4}$$

$$k_2^* t 10^{-k_2^* t} / \left(\frac{P}{P_0} - 10^{-k_2^* t} \right) = z \tag{5}$$

we obtain

$$z = y / (1 - 10^{-y}) \tag{6}$$

The formulae 4–6 were applied in the following way. First, z was calculated from the observed P, t -values and the known value of k_2^* by means of eqn. 5.

Table 4. Hydrolysis of ethyl acetoacetate at 37.0°C in solutions of strong acids (c M).

Hydrochloric acid			Sulphuric acid				Perchloric acid		
c	$k_1 \times 10^5$	$\frac{k_1 \times 10^5}{[H^+]}$	c	$[H^+]$	$k_1 \times 10^5$	$\frac{k_1 \times 10^5}{[H^+]}$	c	$k_1 \times 10^5$	$\frac{k_1 \times 10^5}{[H^+]}$
0.500	2.55	5.10	0.500	0.547	2.99	5.47	0.250	1.19	4.76
1.000	5.55	5.55	1.000	1.07	6.41	5.99	0.500	2.32	4.64
1.333	7.64	5.73	2.000	2.11	15.02	7.12	1.000	4.36	4.36
2.00	12.30	6.15	3.00	3.13	27.8	8.88	2.000	8.50	4.25
3.02	21.08	6.98	4.00	4.14	44.5	11.01	3.00	12.71	4.23
4.00	30.83	7.71	5.00	5.11	68.1	13.32	4.00	17.8	4.44
1.00 ^a	6.79	6.79					5.00	23.3	4.66
1.00 ^b	8.02	8.02					6.00	29.7	4.96

^a The solution contained in addition 1.00 M NaCl.

^b The solution contained in addition 2.00 M NaCl.

Then, y was found by means of a four-place table of function 6 computed for values of y from -1 to $+1$ with intervals of 0.01. Finally, k_1 was found from a plot of y against t , applying eqn. 4.

The rate constants k_1 (in sec^{-1}) found for solutions of hydrochloric, sulphuric, and perchloric acid are given in Table 4. For hydrochloric and perchloric acid $[H^+]$ may with good approximation be set equal to c . For sulphuric acid approximate values of $[H^+]$ were computed from estimates of the two dissociation constants of the acid made by Young and Blatz⁴ mainly on the basis of measurements of the intensities of Raman-lines carried out by Rao⁵. As seen from Table 4, k_1 for hydrochloric and sulphuric acid increases more rapidly than $[H^+]$, while the ratio $k_1/[H^+]$ for perchloric acid at first decreases, then passes a minimum

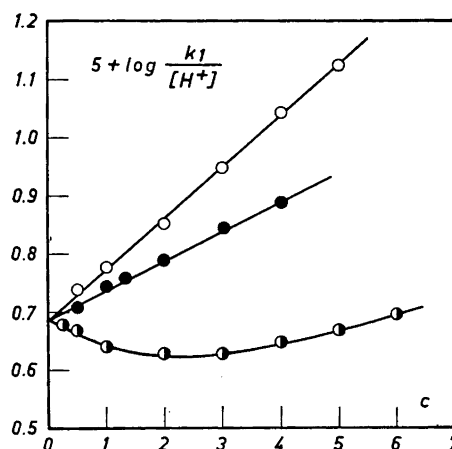


Fig. 1. Plot of $\log(k_1/[H^+])$ against c for the hydrolysis of ethyl acetoacetate in solutions of sulphuric acid (open circles), hydrochloric acid (closed circles), and perchloric acid (semi-closed circles).

(between 2 and 3 M HClO_4), and finally increases. Fig. 1 shows a plot of $\log(k_1/[\text{H}^+])$ for the three acids. For hydrochloric and sulphuric acid, the points fall close to straight lines with equations

$$\begin{array}{ll} \text{for hydrochloric acid} & \log(k_1/[\text{H}^+]) = 0.687 - 5 + 0.051 c \\ \text{for sulphuric acid} & \log(k_1/[\text{H}^+]) = 0.686 - 5 + 0.088 c \end{array}$$

By extrapolation to $c = 0$ is for all three acids obtained

$$k_1 = 4.86 \times 10^{-5} [\text{H}^+] \text{ sec}^{-1}.$$

A similar behaviour of the three acids was found in the hydrolytic decomposition of urethane⁶. Here, however, the value of $k/[\text{H}^+]$ found by extrapolation to $c = 0$ was higher for sulphuric acid than for the two other acids, a result which may possibly be attributed to acid catalysis by the ion HSO_4^- . Since the extrapolation for the hydrolysis of ethyl acetoacetate gives the same value for all three acids, no perceptible catalysis by the ion HSO_4^- is found in this reaction.

If the rate-determining step in ester-hydrolysis is assumed to be a bimolecular reaction between an ester molecule (E) and a *hydrated* hydrogen ion (probably $\text{H}(\text{H}_2\text{O})_4^+$, but here for simplicity written as H^+), the first-order rate constant k may be expressed by the formula

$$k = A[\text{H}^+]f_{\text{E}}f_{\text{H}^+}/f_{\text{EH}^+}$$

where A is a constant, f denotes activity coefficient, and EH^+ the transition state. If, to a first approximation, we set

$$\log(f_{\text{E}}f_{\text{H}^+}/f_{\text{EH}^+}) = Bc$$

where B is a constant, we obtain the approximate formula

$$\log(k/[\text{H}^+]) = \log A + Bc \quad (7)$$

It follows from the experiments in this paper that formula 7 holds for the hydrolysis of ethyl acetoacetate in solutions of hydrochloric acid (up to 4 M) and in solutions of sulphuric acid (up to 5 M) while it fails for the hydrolysis in solutions of perchloric acid. A similar result was earlier⁶ obtained for the hydrolysis of ethyl urethane in solutions of the three acids.

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