The Uncatalysed and the Cupric-Ion Catalysed Decarboxylation of Dihydroxytartaric Acid

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The decomposition of dihydroxytartaric acid into tartronic acid and carbon dioxide was studied kinetically at the temperature 37° C in solutions of hydrochloric acid and in acetate buffer solutions. By an analysis of the experimental data, separate rate constants were determined for each of the three simultaneous reactions: decarboxylation of undissociated dihydroxytartaric acid, of its univalent and divalent ion. It was found that the decomposition of the univalent ion, but not that of the divalent ion, is accelerated by acetate ions. An analogous effect of acetate ions has earlier been found in the decarboxylation of oxaloacetic acid.

It was shown that the decarboxylation of dihydroxytartaric acid, like that of other *dibasic* β-keto carboxylic acids, is catalysed by cupric ions. It was concluded from the experiments that, what appears as a cupric-ion catalysis, is actually a spontaneous decarboxylation of a complex of one cupric ion and one divalent dihydroxytartrate ion. An analogous explanation was earlier given to the cupric ion catalysis in the decarboxylation of oxaloacetic acid.

In the present paper, the decarboxylation of dihydroxytartaric acid

$$HOOC-C(OH)_2-C(OH)_2-COOH \rightarrow HOOC-CHOH-COOH + CO_2 + H_2O$$
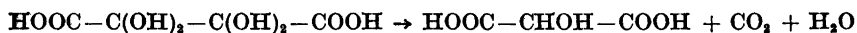
has been studied kinetically at the temperature 37.0° C in solutions of hydrochloric acid and in acetate buffer solutions. All the solutions contained potassium chloride up to a total ionic strength of approximately 0.3. The object of the study was to make out which contribution the spontaneous decomposition of the different molecular species (undissociated acid, uni- and di-valent dihydroxytartrate ion) give to the total rate. It seems to be a general rule that the decarboxylation of dibasic β-keto carboxylic acids is catalysed by certain metal ions, *e. g.* cupric ions [1]. It was therefore of interest to examine whether cupric ions catalyse also the decarboxylation of dihydroxytartaric acid, and an attempt was made to study this question.

The reaction was followed by observing the pressure above the solution by means of an apparatus described earlier [2]. The difference (*P* cm mercury)

between the final pressure reading and the reading at the time t minutes after the reaction was started is proportional to the concentration of dihydroxytartaric acid present in the solution at the time t. A plot of log P against t should therefore, if the reaction is of first order, give a straight line whose slope is $k^* = 0.4343\ k$, where k denotes the rate constant. While the author in earlier papers on rates of reactions has always given k^* *per minute*, the rate constants are in this paper given as k *per second* as recommended by the Commission on Kinetics of Chemical Reactions under the International Union of Pure and Applied Chemistry [3]. Change to the new unit may be carried out by means of the equation

$$k\ (\text{per second}) = 3.838 \times 10^{-2}\ k^*\ (\text{per minute})$$

MATERIALS

Sodium dihydroxytartrate was prepared and purified as described in the previous paper [4]. Owing to the slight solubility of this salt, it could only be used in kinetic experiments where the solution contained an excess of strong acid. The following two preparations of free dihydroxytartaric acid were therefore made.

Dihydroxytartaric acid (preparation 1). Through a mixture of 15 g of sodium dihydroxytartrate and 80 ml of acetone, immersed in an ice bath, was passed a current of dry hydrogen chloride. The precipitate, consisting of sodium chloride and a little unchanged sodium dihydroxytartrate, was isolated by suction on a sintered glass filter. Hydrogen chloride and acetone were removed from the filtrate by distillation in vacuum at room temperature, at last in a desiccator over sulphuric acid and solid potassium hydroxide. The brown residue was extracted with 75 ml of warm acetone. After filtration, the solution was cooled in ice and added 200 ml of benzene. The precipitate was isolated by suction, washed with benzene, and recrystallised once more by the same procedure. It was finally dried in vacuum over paraffin-wax shavings and solid potassium hydroxide.

Dihydroxytartaric acid (preparation 2) was prepared from dihydroxyfumaric acid [5] by the method of Fenton [6]. It was recrystallised in the same way as preparation 1.

Although the two preparations of the acid were kept in a desiccator over concentrated sulphuric acid, they gradually changed into tartronic acid, though with different rates. This follows from the observation that the total pressure increase in the kinetic experiments was too small when the free acid was used instead of the sodium salt, and the discrepancy increased with the age of the preparation, more rapidly for preparation 1 than for preparation 2. The same result is obtained from the following titrations. Samples of preparations 1 and 2 were taken at different time, weighed and dissolved in water. The solutions were left for 24 hours at 37° C, after which time the dihydroxytartaric acid was completely transformed into tartronic acid and carbon dioxide. The latter was removed by a current of carbon-dioxide-free air, and the solution was titrated with sodium hydroxide. From the results the following data were obtained:

	Preparation 1					Preparation 2		
Age of the preparation (days)	9	20	28	39	64	17	36	47
Mole per cent tartronic acid	5	17	26	38	62	0	7	9

Preparation 1 was not more than 35 days old, preparation 2 not more than 50 days old, when used in the kinetic measurements.

The water, hydrochloric acid, and acetic acid used for making up the solutions were redistilled in an all-glass apparatus. The potassium chloride was of analytical purity and was further recrystallised twice from redistilled water. The acetate buffers were prepared from stock solutions of potassium chloride, acetic acid, and potassium acetate. The latter was made by mixing titrated solutions of acetic acid and potassium hydroxide. When a

solution of potassium chloride prepared by neutralising potassium hydroxide with hydro-chloric acid, instead of one made from crystalline potassium chloride, was used for making up the acetate buffer, the same rate constant was obtained. This shows that the potassium hydroxide did not contain perceptible amounts of catalytically active impurities.

THE RATE OF DECOMPOSITION IN SOLUTIONS OF HYDROGEN AND POTASSIUM CHLORIDE

The composition of the solutions examined and the results obtained are shown in Table 1. In the first column, the word Salt indicates that the solution of dihydroxytartaric acid was made, and the reaction started, by dissolving the sodium salt in a solvent containing an excess of hydrochloric acid, while Ac. 1 and Ac. 2 denote that preparation 1 and 2, respectively, of the free acid were dissolved. The initial concentrations x_0 of dihydroxytartaric acid are given in the third column. The ionic strengths of the solutions varied only from 0.301 to 0.307.

Table 1. Decomposition of dihydroxytartaric acid at 37° C.

Prep.	Curve Fig. 1	x_0	HCl	KCl	NaCl	a_1	a_2	$k\ 10^4$ found	$k\ 10^4$ calc.
Salt		0.01374	0.2720		0.027	0.0821	0.00013	0.381	0.380—0.381
Ac. 1		0.01551	0.1997	0.100		0.1083	0.00023	0.489	0.489—0.491
Salt		0.01376	0.1721	0.100	0.028	0.1234	0.00030	0.552	0.552—0.555
Salt		0.01379	0.0722	0.200	0.028	0.2467	0.00138	1.082	1.071—1.087
Ac. 2	II	0.01377	0.0500	0.250		0.3151	0.0025	1.368	1.354—1.405
Salt		0.01373	0.0426	0.230	0.027	0.3450	0.0031	1.517	1.487—1.540
Salt		0.01320	0.0235	0.250	0.026	0.461	0.0069	2.062	1.999—2.113
Salt	I	0.01392	0.0220	0.250	0.028	0.471	0.0073	2.089	2.038—2.169
Ac. 1		0.01367	0.0100	0.290		0.587	0.0149	2.72	2.59 —2.83
Ac. 2		0.01372	0.0100	0.290		0.587	0.0149	2.72	2.59 —2.83
Ac. 2	III	0.01380		0.300		0.708	0.0342	3.67	3.35 —3.75
Ac. 1	IV	0.01380		0.300		0.708	0.0342	3.65	3.35 —3.75

If the hydrogen ion concentration is constant, we may expect a reaction of first order with the constant

$$k = k_0\ (1—\alpha_1—\alpha_2) + k_1\ \alpha_1 + k_2\ \alpha_2 \qquad (1)$$

where k_0, k_1, and k_2 are rate constants for the spontaneous decomposition of undissociated dihydroxytartaric acid, univalent and divalent ion, respectively, while α_1 and α_2 denote the degrees of dissociation into uni- and di-valent ion, respectively. Since tartronic acid is weaker than dihydroxytartaric acid, the hydrogen ion concentration will actually decrease during the reaction. A departure from the first-order law may therefore be expected, especially when little or no hydrochloric acid is present. No significant deviation from the first-order law could, however, be detected in those experiments where the solution was made by dissolving the sodium salt. In Fig. 1, Curve 1, is shown
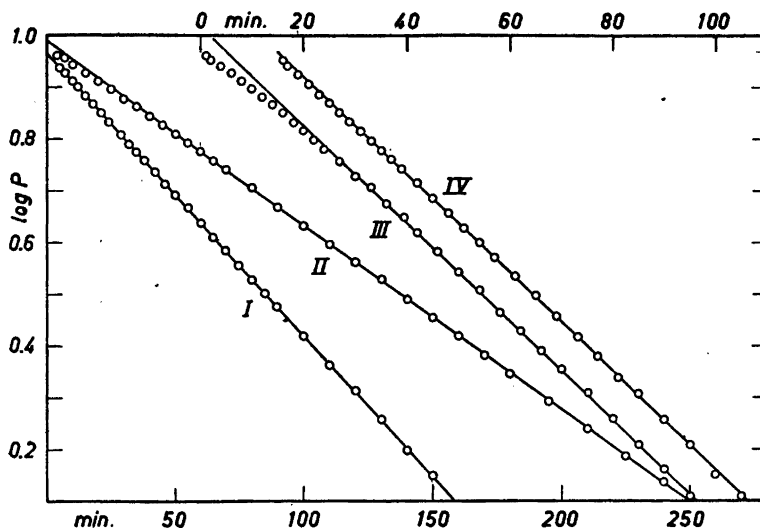
Fig. 1. Plots of log P *against* t *for four of the experiments presented in Table 1. The time scale for Curves I and II is given at the bottom, that for Curves III and IV at the top. Curve IV has been displaced a length corresponding to 15 minutes to the right.*

a plot of log P against t for that solution where the largest deviation should be expected. When the free acid was dissolved instead of the sodium salt, a systematic deviation, larger for preparation 2 than for preparation 1, was found in the initial stages of the reaction as shown in Fig. 1, Curves II—IV. This deviation could, however, not be explained by the change in α_1 and α_2 due to the formation of tartronic acid. Except in the first part of the reaction, the points fell, also here, close to straight lines, from which the rate constants k given in the next to the last column of Table 1 were computed.

The degrees of dissociation α_1 and α_2 of dihydroxytartaric acid, both those corresponding to the initial and to the final composition of the solutions, were computed by means of the dissociation constants of dihydroxytartaric acid and tartronic acid found in the previous paper [4]. Since the dissociation constants of dihydroxytartaric acid were not measured at 37° C, those corresponding to 25° C were applied. The values used were: for dihydroxytartaric acid $K_1 = 2.44 \times 10^{-2}$ and $K_2 = 4.2 \times 10^{-4}$, for tartronic acid $K_1 = 9.02 \times 10^{-3}$ and $K_2 = 8.1 \times 10^{-5}$. The degrees of dissociation presented in Table 1 are averages of those calculated for the initial and final composition of the solutions. Equation 1 was then applied to the experimental data. For k_2 was chosen the value 17.7×10^{-4} obtained from experiments on acetate buffers. The best agreement with the measurements was found when

$\qquad k_0 = 0.041 \times 10^{-4} \ sec^{-1} \qquad$ and $\qquad k_1 = 4.15 \times 10^{-4} \ sec^{-1}$

By means of eqn. (1) and the data for k_0, k_1, and k_2 given here, we may calculate k when α_1 and α_2 are known. In the last column of Table 1 are given two values for each solution, the former has been calculated for the initial, the latter

for the final composition of the solution. The value of k obtained directly from the measurements is always within the interval determined by the two calculated values. When the last two experiments are excepted, it is always very close to their average.

THE RATE OF DECOMPOSITION IN ACETATE BUFFER SOLUTIONS

The reaction was started by dissolving free dihydroxytartaric acid in solutions containing acetic acid, potassium acetate, and potassium chloride. The experiments presented in Table 2 were all carried out with preparation 1 of the acid. They agreed well with the first-order law. A plot of $\log P$ against t for the solution having the smallest buffer capacity (the last one in Table 2) is shown in Fig. 2, Curve V. When preparation 2 was used instead of preparation 1, a rather large deviation from first-order was observed in the first part of the reaction (similar to that shown in Fig. 1, Curves II—IV), but the points approached a straight line having the same slope as that found for preparation 1. No explanation can be given to the different initial rates of the two preparations.

Table 2. Decomposition of dihydroxytartaric acid (initial concentration 0.0146 molar) at 37° C in the solvent: a molar acetic acid, b molar potassium acetate, (0.300 — b) molar potassium chloride.

a	b	[HAc]	[Ac$^-$]	a_1	k 10^4 found	k 10^4 calc.	k_1 10^4	k_2 10^4
0.400	0.300	0.426	0.274	0.106	17.28	17.31		
0.200	0.300	0.227	0.273	0.059	17.48	17.46		
0.100	0.300	0.128	0.272	0.034	17.56	17.53	14.5	17.64
0.040	0.300	0.068	0.272	0.019	17.55	17.58		
0.400	0.200	0.424	0.176	0.155	16.79	16.77		
0.200	0.200	0.226	0.174	0.090	17.09	17.11		
0.100	0.200	0.127	0.173	0.053	17.29	17.30	12.4	17.58
0.040	0.200	0.068	0.172	0.029	17.44	17.43		
0.300	0.100	0.323	0.077	0.242	15.39	15.39		
0.200	0.100	0.224	0.076	0.183	15.97	15.98		
0.100	0.100	0.125	0.075	0.113	16.77	16.69	7.7	17.83
0.040 [a]	0.100	0.067	0.073	0.065	17.09	17.17		

[a] The kinetic data for this solution are shown in Fig. 2, Curve V.

In order to compute k_1 and k_2 from the experimental data, we apply eqn. (1). When the small amount of undissociated dihydroxytartaric acid present in the solution is neglected, the equation may be written

$$k = k_2 — (k_2 — k_1)\ a_1 \tag{2}$$

The hydrogen ion concentration of the solution decreases slightly when dihydroxytartaric acid is transformed into tartronic acid. α_1 was therefore computed both for the initial and the final composition of the solution. The values of α_1 given in Table 2 are averages of the two values. The concentrations of undissociated acetic acid [HAc] and the acetate ion concentration [Ac⁻] given in the third and fourth column of the table are also those corresponding to an average composition of the solution. In the computation of α_1, the dissociation constants of dihydroxytartaric and tartronic acid given earlier in this paper were used, while for acetic acid was chosen $K = 3.20 \times 10^{-5}$ (estimated [7] for 0.3 molar sodium chloride as solvent from measurements by Harned and Hickey [8]). Owing to inaccuracies in the dissociation constants applied, the values of α_1 given in the table may all be either a little too high or a little too low. This will not perceptibly affect the value found for k_2, since this constant is determined by a short extrapolation to $\alpha_1 = 0$ by means of eqn. (2). It may, however, have an appreciable influence in the computation of k_1, but the determination of k_1 from experiments on acetate buffer solutions is already less accurate since here α_1 is always much smaller than α_2.

Within each of the three series of solutions presented in Table 2, the acetate ion concentration is nearly constant. Applying eqn. (2) to each series separately, we compute the values of k_1 and k_2 given in the last two columns of the table. When they are introduced into eqn. (2), and k is calculated, the values given in the seventh column are obtained. When the three series of measurements are compared, it is seen that k_2 is independent of the acetate ion concentration. The average value for all three series is $k_2 = 17.7 \times 10^{-4}$ sec⁻¹. The values of k_1 increase, however, with increasing acetate ion concentration as shown in the following lines

[Ac⁻]	0	0.075	0.174	0.273
k_1 10⁴	4.15	7.7	12.4	14.5
$\Delta k_1 10^4/[Ac^-]$		47	47	38

An analogous effect was found in the decarboxylation of oxaloacetic acid [7]. Also here, the rate constant for the decomposition of the divalent ion was independent of the acetate ion concentration, while that for the decomposition of the univalent ion increased with increasing acetate ion concentration, although relatively less than in the case of dihydroxytartaric acid.

The rate constants for the spontaneous decarboxylation of four β-keto carboxylic acids and their ions at 37° C are, for comparison, given in Table 3. Their dissociation constants are shown in the last two columns of the table.

CUPRIC-ION CATALYSIS

The solutions examined contained hydrogen chloride, potassium chloride, and cupric nitrate, and the reaction was started by adding sodium dihydroxytartrate. It was found that cupric ions have a large catalytic effect, which increases rapidly with decreasing hydrogen ion concentration. The kinetics of the reaction was, however, except in the most acid solutions examined, too

Table 3. *Rate of decarboxylation of some β-keto carboxylic acids. k_0, k_1, and k_2 are the rate constants in sec^{-1} for the spontaneous decarboxylation of the undissociated acid, the univalent ion, and the divalent ion, respectively, at the temperature 37° C. K_1 and K_2 are the first and second dissociation constant of the acid at 25° C and zero ionic strength.*

	k_0 10^4	k_1 10^4	k_2 10^4	K_1 10^3	K_2 10^4
Dihydroxytartaric acid [a]	0.041	4.15	17.7	11.3	0.99
Oxaloacetic acid [a]	0.068	2.48	0.695	2.79	0.427
Acetoacetic acid [b]	0.80	0.0148		0.27	
Dimethylacetoacetic acid [c]	3.15	0.0091	.	0.31	

[a] The rate constants are for the solvent 0.3 M KCl. Pedersen [4,7,9] and this paper.
[b] Ljunggren [10], Pedersen [11].
[c] The rate constants are extrapolated to 37° from data at 25° and 35° C. Pedersen [12].

complicated to make an analysis of the data seem promising. An attempt to give a partial interpretation of the kinetic data was therefore only made for the two series of measurements presented in Table 4. When log P in these experiments was plotted against t, it was only within a limited range that the points did not deviate systematically from a straight line. Before this interval the points were below, after it they were above the straight line. This is shown in Fig. 2, Curves VI and VII, for two of the solutions in Table 4. In the fourth column of the table is shown how many per cent of the dihydroxytartaric acid
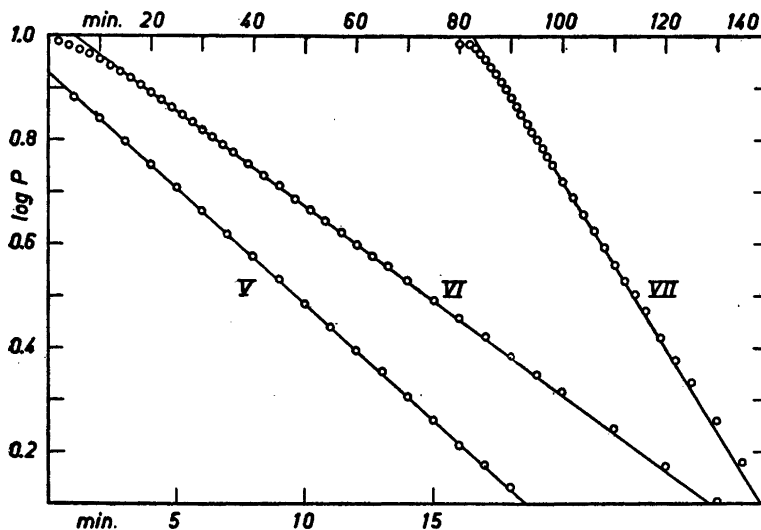
Fig. 2. *Plots of log P against t for one experiment in Table 2 (Curve V) and for two experiments in Table 4 (Curves VI and VII). The time scale for Curve V is given at the bottom, that for Curves VI and VII at the top. Curve VII has been displaced a length corresponding to 80 minutes to the right.*

Table 4. Cupric ion catalysis in the decarboxylation of dihydroxytartaric acid (initial concentration 0.014 M) at 37° C.

Solvents. A: 0.2720 M HCl, 0.028 M NaCl, c molar $Cu(NO_3)_2$
B: 0.1721 M HCl, 0.100 M KCl, 0.028 M NaCl, c molar $Cu(NO_3)_2$

Solvent	c	Curve in Fig. 2	Range %	$k \cdot 10^4$	$k_c \cdot 10^4$	$\dfrac{k_c}{c} \cdot 10^2$	$a_2 \cdot 10^4$	$\dfrac{k_c}{ca_2}$
A	0.00000			0.381	0.000		1.27	
A	0.00100		6 − 60	0.855	0.474	4.74		373
A	0.00200		6 − 70	1.328	0.947	4.74		
A	0.00500	VI	20 − 80	2.79	2.41	4.82		
A	0.01000		37 − 83	5.33	4.95	4.95		
A	0.1000		30 − 95	46.9	46.5	4.65		
B	0.00000			0.552	0.00		2.99	
B	0.00200		10 − 43	2.79	2.24	11.2		375
B	0.00500	VII	20 − 65	6.19	5.64	11.3		
B	0.01000		70 − 95	11.0	10.4	10.4		

was decomposed at the beginning and at the end of the range within which the first-order law was obeyed. The rate constants k given in the fifth column were computed in the usual way from the slopes of the straight lines. When the value of k found for the solvent without cupric nitrate was subtracted, the rate constant k_c for the pure cupric ion catalysis was obtained. It is seen from the table that k_c is, in both series, nearly proportional to the cupric ion concentration c, but the proportionality factor k_c/c increases with decreasing hydrogen ion concentration. As shown in the last column of the table, k_c/ca_2 has, however, the same value in both series. It is therefore reasonable to conclude that, what appears as a cupric-ion catalysis, is actually a spontaneous decarboxylation of a complex CuT of one cupric ion and one divalent dihydroxytartrate ion, T^{--}. When x denotes the analytical concentration of dihydroxytartaric acid, k_{CuT} the rate constant for the spontaneous decarboxylation of the complex CuT, and K_{CuT} the complexity constant, we have

$$k_c\ x = k_{CuT}\ [CuT] = k_{CuT}\ K_{CuT}\ c\ a_2\ x$$

Hence,

$$k_c/ca_2 = k_{CuT}\ K_{CuT}$$

It therefore follows from the data in Table 4 that the product of the rate constant for the spontaneous decarboxylation of the cupric-dihydroxytartrate complex and its complexity constant is about 374 $sec^{-1}mole^{-1}$ l at the temperature 37° C and the ionic strength 0.3.

An analogous explanation was in an earlier paper [1] given to the cupric-ion catalysis in the decarboxylation of oxaloacetic acid. The catalysis was here explained as being the result of a spontaneous decarboxylation of a complex CuOx of one cupric ion and one oxaloacetate ion, Ox^{--}. The reaction was studied at 37° C and at ionic strengths up to 0.206. The values found for the product of the rate constant k_{CuOx} for the spontaneous decarboxylation of the

complex CuOx and its complexity constant K_{CuOx} were, when recalculated to the units used in the present paper:

Ionic strength	0.053	0.104	0.206	(0.3)
$k_{CuOx}K_{CuOx}(\text{sec}^{-1}\text{mole}^{-1}\text{l})$	1 080	690	421	(360)

The value of the product corresponding to the ionic strength 0.3 was found by extrapolation. It is interesting to note that the product of the rate constant and the complexity constant is nearly the same for the cupric-dihydroxytartrate and the cupric-oxaloacetate complex. For the latter it was possible to give approximate values of the two factors. It was found that the rate constant for the decarboxylation of the cupric-oxaloacetate complex k_{CuOx} is about 5.8×10^{-2} sec^{-1} independently of the ionic strength. If the complexity constants for the two complexes are of the same order of magnitude, the rate constants for their decarboxylation will also be of the same order of magnitude.

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