436. *The Kinetics of the Metal-ion Catalysed Decarboxylation of Acetonedicarboxylic Acid.*

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The rate of decarboxylation of acetonedicarboxylic acid has been studied over a range of pH and in the presence of various catalytically active metal ions. The undissociated acid, the univalent ion, and the bivalent ion are all decarboxylated at different rates, and it is the rate of decomposition of the bivalent ion which is most strongly influenced by metal ions. Catalytic constants for the various ions are given. The mechanism of the reaction is discussed, and it is concluded that catalysis depends on chelation between the activated complex and a metal ion.

THE kinetics of many reactions showing specific hydrogen-ion and general acid catalysis have been investigated in detail, but few reactions have been studied where metal ions act as catalysts. Apart from reactions where ions of variable valency function as electron carriers, metal ions might be expected to display a more general type of catalytic effect owing to their electrophilic powers which are in many ways analogous to those of the proton (cf. Bjerrum, *Chem. Reviews*, 1950, **46**, 381).

The catalysis of the decarboxylation of acetonedicarboxylic acid by metal ions appears to have first been observed by Krebs (*Biochem. J.*, 1942, **36**, 303). Wiig (*J. Phys. Chem.*, 1928, **32**, 961) studied the spontaneous and amine-catalysed decarboxylation of this acid. He found the spontaneous reaction to be of first order, the rate reaching a constant minimal value with increasing concentration of hydrogen ion in solution. The reaction was written: $HO_2C{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CO_2H \longrightarrow CH_3{\cdot}CO{\cdot}CH_3 + 2CO_2$. There were, however, certain complexities in Wiig's results and it will be seen later that his views concerning the mechanism of the reaction cannot be sustained.

EXPERIMENTAL

Acetonedicarboxylic acid, prepared from citric acid and fuming sulphuric acid (Ingold and Nickolls, *J.*, 1922, **121**, 1642) was recrystallised three times from ethyl acetate and stored over phosphoric oxide in a vacuum-desiccator. It was stable and melted sharply with decomposition at 135°; impure samples rapidly decomposed with loss of carbon dioxide. Titration of the pure sample against sodium hydroxide gave the theoretical end-point. The approximate values of the dissociation constants calculated from the titration curve at room temperature measured with a commercial pH meter are $K_1 = 1{\cdot}8 \times 10^{-3}$ and $K_2 = 1{\cdot}9 \times 10^{-4}$. Hence the unbuffered solution contains undissociated acid and univalent ions, whilst in an acetate buffer of $[H^+] < 3 \times 10^{-5}$ the acid is almost entirely converted into the bivalent ion. The other chemicals used were of " AnalaR " quality; all solutions were made up with doubly distilled water, the second distillate being collected through a quartz condenser. Solutions of metallic salts were standardised when necessary with standard sodium ethylenediaminetetra-acetate, the methods of Schwarzenbach *et al.* being used (for references see Irving, *Ann. Reports*, 1949, **46**, 273).

The kinetics of the decarboxylation were conveniently investigated at 42° ± 0·02°, the reaction being followed by measuring the pressure of carbon dioxide evolved in an apparatus similar to that used by Bell and Trotman-Dickenson (*J.*, 1949, 1288). In an unbuffered solution each molecule of acetonedicarboxylic acid loses two molecules of carbon dioxide, but in an acetate buffer the second molecule of carbon dioxide is lost very slowly. The reason is that loss of one molecule of carbon dioxide produces acetoacetic acid, which in an acetate buffer is almost completely converted into the ion. A short extrapolation of Ljunggren's results (Diss., Lund, 1925; quoted by Pedersen, *J. Amer. Chem. Soc.*, 1929, **51**, 2098) shows that the acetoacetate ion decomposes 55 times more slowly than the undissociated acid at 42°, and hence the very slow loss of the second molecule of carbon dioxide under these conditions is explained. The spontaneous and metal-ion catalysed decarboxylation was studied in acetate buffer solutions, for which accurate values of the hydrogen-ion concentration at various buffer concentrations are calculable from Harned and Hickey's data (*ibid.*, 1937, **59**, 1284, 2303). A few measurements were also made with unbuffered solutions for comparison with Wiig's results and to determine the effect of pH on the metal-ion catalysis. All solutions were made up by weight, 5 ml. of a solution with an initial concentration of acetonedicarboxylic acid of 0·027M being used for each experiment; in unbuffered and acid solutions the initial concentration was halved, since the volume of carbon dioxide evolved is twice as great. The solutions were made up to a constant ionic strength of 0·6, usually with potassium chloride, but in experiments involving lead, cadmium, and zinc salts, potassium nitrate was used instead; cadmium and zinc ions form rather stable complexes with chloride ions (Bjerrum, *loc. cit.*).

RESULTS AND DISCUSSION

(a) *Measurements in Acetate Buffer Solutions.*—The slow decomposition of the acetoacetate ion formed caused a slight curvature of the first-order plots obtained by Guggenheim's method (*Phil. Mag.*, 1926, **7**, 538). Corrected first-order constants were evaluated as follows. The kinetic scheme may be written as

$$H_2O + {}^-O_2C{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CO_2^- \xrightarrow{k_1} CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO_2^- + CO_2 + OH^-$$

$$H_2O + CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO_2^- \xrightarrow{k_2} CH_3{\cdot}CO{\cdot}CH_3 + CO_2 + OH^-$$

It can easily be shown that the amount of carbon dioxide h produced after time t is given by

$$h = [a/(k_2 - k_1)]\{2(k_2 - k_1) - (2k_2 - k_1)e^{-k_1t} + k_1e^{-k_2t}\} \quad . \quad . \quad . \quad (1)$$

where a is the initial concentration of the acetonedicarboxylate ion. Now, according to Ljunggren (*loc. cit.*), k_2 is $1{\cdot}6 \times 10^{-4}$ min.$^{-1}$, and since in these experiments $t \ll 1/k_2$ terms higher than k_2t may be neglected in the expansion of e^{-k_2t}. This gives

$$h = 2a - \frac{(2k_2 - k_1)}{(k_2 - k_1)}\, ae^{-k_1t} + \frac{k_1a}{(k_2 - k_1)}\,(1 - k_2t) \quad . \quad . \quad . \quad . \quad (2)$$

In Guggenheim's method each reading at time t is considered in conjunction with a reading at a time $t + \tau$, where τ is a suitably chosen interval. Hence

$$h' = 2a - \frac{(2k_2 - k_1)}{(k_2 - k_1)}\, a\, e^{-k_1(t+\tau)} + \frac{k_1a}{(k_2 - k_1)}\,[1 - k_2(t + \tau)] \quad . \quad . \quad (3)$$

Combining (2) and (3) and remembering that $(h' - h)$ is proportional to $(r' - r)$ where r' and r are the corresponding manometer readings, we get

$$\log_{10}[(r' - r) + A] = B - k_1t/2{\cdot}303 \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where A and B are unknown constants for a given experiment, both involving k_1 and k_2.

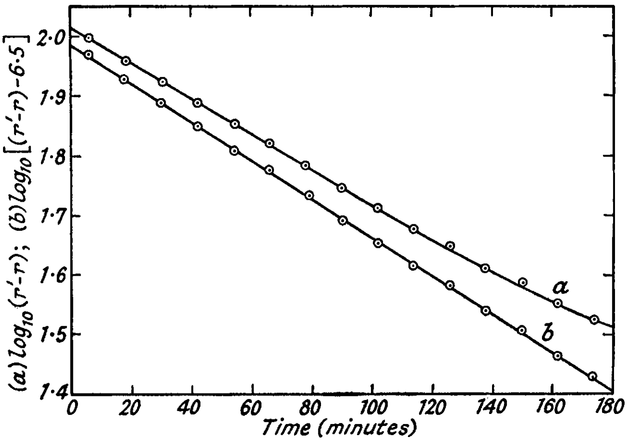
Hence, if a value of A is found such that a plot of the left-hand side of equation (4) against t is linear, the slope of the straight line gives k_1. Now (4) may be rewritten as

$$\log_{10}(r' - r) + A/2{\cdot}303(r' - r) = B - k_1t/2{\cdot}303 \quad . \quad . \quad . \quad . \quad (5)$$

since $A/[2{\cdot}303(r' - r)] = kk_2A\tau/[2{\cdot}303(h' - h)(k_2 - k_1)] \ll 1$

An approximate value of k_1 was determined from the initial slope of the plot of $\log_{10}(r' - r)$ against t, and A was estimated by plotting $\log_{10}(r' - r) + kt/2{\cdot}303$ against $1/(r' - r)$. This value of A was then used to compute $\log_{10}(r' - r) + A/2{\cdot}303(r' - r)$, which when plotted against t gave an improved value of k_1. This procedure was repeated until values of k_1 and A satisfying equation (4) were obtained. The revised value of k_1 never differed from the approximate one by more than 7%. In the more strongly metal-ion catalysed decompositions there was no deviation of the original plot from linearity, since the decarboxylation of the acetoacetate ion is not catalysed by metal ions. Fig. 1 shows a typical original and corrected first-order plot. The accuracy of the first-order constants obtained is estimated as ±2%.

FIG. 1.



Catalysis by hydrogen ions. Table 1 gives the values of the rate constants obtained over a range of hydrogen-ion concentrations, which were calculated by using a value of $3{\cdot}30 \times 10^{-5}$ for the concentration dissociation constant of acetic acid at 42° and $I = 0{\cdot}6$ (calculated from Harned and Hickey's data, *loc. cit.*), and are mean values corresponding to 50% decomposition of the acetonedicarboxylic acid added (initially 0·027m). In the first instance the acid was assumed to be completely dissociated; then, a preliminary value for the second dissociation constant having been obtained, the values of the hydrogen-ion concentrations recorded were computed. The correction never exceeded 5%. The first-order rate constant increases with increasing hydrogen-ion concentration, but not linearly. If both the bivalent ion and the univalent ion decompose, the observed velocity constant may be written as

TABLE 1. (Concns. in moles/kg. of solution.)

[AcOH]	0·138	0·236	0·429	0·622	0·811	0·427	0·618	0·813
[AcONa]	0·352	0·351	0·353	0·353	0·351	0·157	0·161	0·160
$10^5[H^+]$	1·31	2·22	4·02	5·83	7·64	9·00	12·70	16·80
$10^3k_1/2{\cdot}303$ (obs.) ...	1·12	1·57	2·23	2·90	3·44	3·81	4·70	5·31
$10^3k_1/2{\cdot}303$ (calc.) ...	1·14	1·55	2·27	2·90	3·44	3·80	4·65	5·39

$$k_1 = k_{A^=}\alpha_{A^=} + k_{HA^-}\alpha_{HA^-}$$

where $\alpha_{HA^-} = 1 - \alpha_{A^=}$, the fraction of the bivalent acetonedicarboxylate ions converted into univalent ions, is equal to $[H^+]/(K_2 + [H^+])$, where K_2 is the second dissociation constant of acetonedicarboxylic acid. Hence

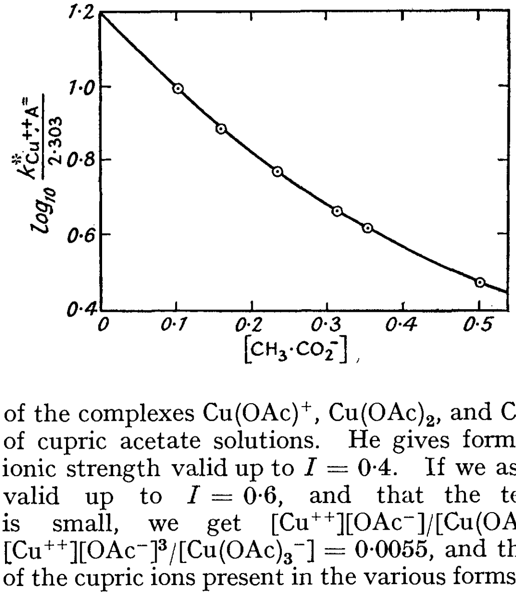
$$k_1 = k_{A^=} + (k_{HA^-} - k_{A^=})[H^+]/(K_2 + [H^+]) \quad . \quad . \quad . \quad . \quad . \quad (6)$$

A short extrapolation of a plot of k_1 against $[H^+]$ to $[H^+] = 0$ gives $k_{A^=} = 1{\cdot}15 \times 10^{-3}$ min.$^{-1}$ and a set of simultaneous equations in two unknowns, k_{HA^-} and K_2 can then be written. Graphical solution gives $k_{HA^-} = 26{\cdot}5 \times 10^{-3}$ and $K_2 = 2{\cdot}10 \times 10^{-4}$. These values being used, the calculated values of k_1 agree with the observed values within the estimated experimental error. Hence the univalent ion decomposes 23 times faster than the bivalent ion; the reaction is an example of specific hydrogen-ion catalysis. The value for K_2 is close to the approximate value determined from the titration curve of the acid at room temperature (p. 2331).

Catalysis by cupric ions. Cupric ions exert a powerful catalytic effect, and the first-order plots were all strictly linear. Section (i) of Table 2 refers to a series of measurements in which the cupric-ion concentration was varied, both the hydrogen-ion and acetate-ion concentration being kept constant. The rate constant may be written as

$$k_1 = k_{A^=}\alpha_{A^=} + k_{HA^-}\alpha_{HA^-} + k^*_{Cu^{++}.A^=}\alpha_{A^=}[Cu^{++}] \quad . \quad . \quad . \quad . \quad (7)$$

Fig. 2.



The values obtained for $k^*_{Cu^{++}.A^=}$, the apparent catalytic constant of the cupric ion, are satisfactorily constant. In the experiments of Section (ii) of Table 2, the acetate-ion concentration was varied, the ionic strength being kept at 0·6 throughout by varying the chloride-ion concentrations. The value of $k^*_{Cu^{++}.A^=}$ is seen to be dependent on the acetate-ion concentration, and Fig. 2 is a plot of $\log_{10} k^*_{Cu^{++}.A^=}$ against the acetate-ion concentration (an average value of $k^*_{Cu^{++}.A^=}$ has been taken where more than one measurement was made at a given acetate-ion concentration). The points lie on a smooth curve which extrapolates to give a value $k^*_{Cu^{++}.A^=} = 36{\cdot}4$ at $[OAc^-] = 0$. The cupric ion is known to form complexes with the acetate ion and Pedersen (*Kgl. Danske Vid. Selsk., Mat. Fys. Medd.*, 1945, **22**, No. 12) has determined values at 18° for the dissociation constants of the complexes $Cu(OAc)^+$, $Cu(OAc)_2$, and $Cu(OAc)_3^-$ by examining the optical properties of cupric acetate solutions. He gives formulæ for the dependence of the constants on ionic strength valid up to $I = 0{\cdot}4$. If we assume that his formulæ will be approximately valid up to $I = 0{\cdot}6$, and that the temperature dependence of the constants is small, we get $[Cu^{++}][OAc^-]/[Cu(OAc)^+] = 0{\cdot}030$, $[Cu^{++}][OAc^-]^2/[Cu(OAc)_2] = [Cu^{++}][OAc^-]^3/[Cu(OAc)_3^-] = 0{\cdot}0055$, and the values recorded in Table 2 for the fraction of the cupric ions present in the various forms. Expressing the apparent catalytic constant of the cupric ions as

$$k^*_{Cu^{++}.A^=} = k_{Cu^{++}.A^=}\alpha_{Cu^{++}} + k_{CuOAc^+.A^=}\alpha_{CuOAc^+} + \\ k_{Cu(OAc)_2.A^=}\alpha_{Cu(OAc)_2} + k_{Cu(OAc)_3^-.A^=}\alpha_{Cu(OAc)_3^-} \quad (8)$$

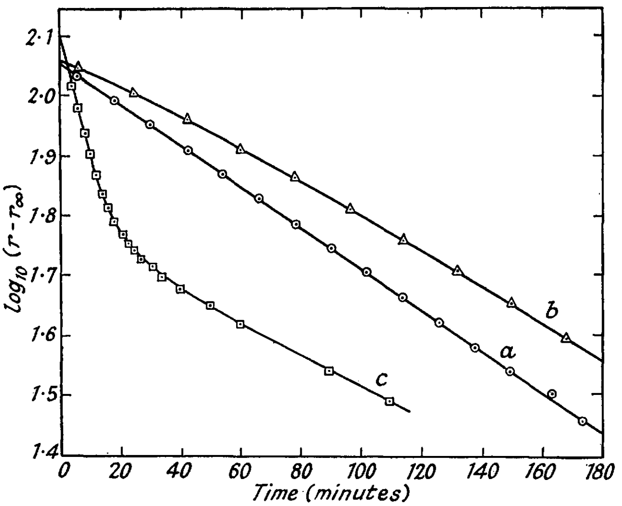
and solving the sets of simultaneous equations, we get $k_{Cu^{++}.A^=} = 36{\cdot}4$, $k_{CuOAc^+.A^=} = 30{\cdot}8$, and $k_{Cu(OAc)_2.A^=} = k_{Cu(OAc)_3^-.A^=} = 0$. The values $k^*_{Cu^{++}.A^=}$ (calc.) of Table 2 are computed by using these coefficients. The quantitative agreement could probably be improved by small adjustments in the dissociation constants of the cupric acetate complexes and the catalytic constants; the value $k_{Cu^{++}.A^=} = 36{\cdot}4$ agrees with the value obtained by

TABLE 2.

	(i)					(ii)					
$10^3[Cu^{++}]$	1·91	4·87	5·90	6·19	7·84	5·80	5·75	5·89	2·90	5·85	5·90
[AcOH]	0·429	0·429	0·429	0·429	0·429	0·425	0·428	0·429	0·429	0·429	0·430
[AcONa]	0·353	0·353	0·353	0·353	0·353	0·101	0·158	0·234	0·311	0·313	0·502
$10^5[H^+]$	4·02	4·02	4·02	4·02	4·02	13·90	8·97	6·06	4·56	4·54	2·83
$10^3k_1/2{\cdot}303$	8·70	18·8	22·7	24·0	29·0	38·8	34·1	29·4	13·6	24·4	17·3
$k^*_{Cu^{++}.A^=}/2{\cdot}303$ (obs.)	4·06	4·06	4·14	4·21	4·07	9·89	7·62	5·82	4·71	4·59	2·98
$\alpha_{Cu^{++}}$	0·024	0·024	0·024	0·025	0·025	0·171	0·094	0·051	0·030	0·031	0·012
$\alpha_{Cu(OAc)^+}$	0·271	0·276	0·276	0·277	0·279	0·531	0·466	0·379	0·302	0·308	0·197
$\alpha_{Cu(OAc)_2}$	0·520	0·520	0·521	0·520	0·520	0·274	0·386	0·477	0·511	0·504	0·531
$\alpha_{Cu(OAc)_3^-}$	0·184	0·181	0·178	0·179	0·177	0·026	0·052	0·102	0·158	0·157	0·259
$k^*_{Cu^{++}.A^=}/2{\cdot}303$ (calc.)	4·02	4·08	4·08	4·11	4·13	9·82	7·73	5·89	4·52	4·62	2·83

extrapolating the curve in Fig. 3 to $[OAc^-] = 0$. Thus both the free cupric ion and the first complex with acetate ion are catalytically active, whilst the neutral and the negatively charged complex exert no catalytic effect. In contrast to the catalysis by hydrogen ions, which is specific, there is a " general " catalysis by cupric ions and at least one of its complexes.

FIG. 3.



(*a*) *Unbuffered*; (*b*) [HCl] = 0·1; (*c*) *Unbuffered*, $[Cu^{++}] = 0{\cdot}058$.

Catalysis by other metal ions. Measurements were made over a range of metal-ion concentrations and, except with aluminium and beryllium, the catalytic constants found are independent of concentration. The catalytic constants for aluminium and beryllium fall off with increasing concentration; this may be due to complex formation between the acetonedicarboxylate ion and the metal ion, but since the pH of an acetate buffer is comparable with the pK values for the aluminium and beryllium aquo-cations, these ions will be partly converted into the corresponding bases and the situation becomes very complex. The values for the catalytic constants of these two ions are therefore only approximate. There is a small variation of catalytic constant with acetate-ion concentration for nickel and zinc, presumably owing to weak complex formation between the metal ion and the acetate ion; for comparative purposes the catalytic constants have been extrapolated to $[OAc^-] = 0$.

The catalytic constants in Table 3 and for the other metal ions studied are collected together in Table 4. The constant for the hydrogen ion is equal to k_{HA^-}/K_2 since the appropriate term in the rate equation may be written as either $k_{HA^-}[AH^-]$ or $k_{H^+.A^=}[A^=][H^+]$

with $[A^=][H^+]/[HA^-] = K_2$. The term refers to the rate of decomposition of an activated complex composed of a bivalent acetonedicarboxylate ion, a proton, and an indeterminate number of water molecules. Similarly for the metal-ion catalysis, a pre-equilibrium involving complex formation is only relevant in so far as it alters the concentrations of anion and metal ion. The absence of variation of catalytic constant with concentration of metal ion shows that the degree of complex formation must be small, and this is confirmed by the very small displacements of the titration curve of the acid at room temperature caused by the presence of metal ions.

(b) *Measurements in Unbuffered and Acid Solutions.*—Each molecule of acetonedicarboxylic acid loses two molecules of carbon dioxide in a reaction which is accurately of the first order (Fig. 3), with $k = 7{\cdot}9 \times 10^{-3}$ min.$^{-1}$. Wiig (*loc. cit.*) does not state the units of the first-order rate constants he records and Moelwyn-Hughes (" Kinetics of Reactions in Solution," Oxford, 1947, p. 32) presumes the quoted values to be in sec.$^{-1}$. If it is assumed they are in min.$^{-1}$, the value at 42° interpolated from Wiig's data at 40° and 50° is $7{\cdot}2 \times 10^{-3}$ which is in fair agreement with the value found in this work. Wiig assumed that two molecules of carbon dioxide are simultaneously lost. This is kinetically equivalent to a slow rate-determining loss of the first molecule followed by rapid loss of the second from the acetoacetic acid produced, *i.e.*, $k_1 \ll k_2$. However, this cannot be true, since the value for the rate constant of the decomposition of acetoacetic acid at this temperature is, according to Ljunggren (*loc. cit.*), $k_2 = 8{\cdot}7 \times 10^{-3}$ min.$^{-1}$. This being so, reference to equation (1) shows that first-order kinetics can only arise if $k_1 = 2k_2$, in which event equation (1) becomes

$$h = 2a - 2ae^{-k_2t} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

This situation, giving a first-order reaction with an apparent rate constant $k = k_2 = k_1/2$,

TABLE 3. *Catalysis by other metal ions.*

$10^2[\text{Ni}^{++}]$	0·909	1·84	2·75	3·66	3·68	3·74
[AcOH]	0·429	0·429	0·429	0·429	0·430	0·432
[AcONa]	0·353	0·353	0·353	0·353	0·254	0·162
$10^5[\text{H}^+]$	4·02	4·02	4·02	4·02	5·60	8·82
$10^3k_1/2{\cdot}303$	3·13	4·12	5·11	6·04	6·59	7·50
$10^2k_{\text{Ni}^{++}.\text{A}^=}/2{\cdot}303$	11·8	12·2	12·5	12·4	13·0	13·8

$10^2[\text{Zn}^{++}]$	1·55	2·70	3·88	3·89	3·88
[AcOH]	0·429	0·429	0·429	0·428	0·427
[AcONa]	0·353	0·353	0·353	0·253	0·159
$10^5[\text{H}^+]$	4·02	4·02	4·02	5·60	8·89
$10^3k_1/2{\cdot}303$	3·36	4·20	5·03	5·54	6·33
$10^2k_{\text{Zn}^{++}.\text{A}^=}/2{\cdot}303$	8·7	8·7	8·6	8·9	9·2

$10^2[\text{Co}^{++}]$	1·95	2·73	3·88
[AcOH]	0·429	0·429	0·429
[AcONa]	0·353	0·353	0·353
$10^5[\text{H}^+]$	4·02	4·02	4·02
$10^3k_1/2{\cdot}303$	3·69	4·30	5·20
$10^2k_{\text{Co}^{++}.\text{A}^=}/2{\cdot}303$	8·9	9·0	9·1

$10^2[\text{La}^{+++}]$	1·91	1·91
[AcOH]	0·429	0·427
[AcONa]	0·353	0·160
$10^5[\text{H}^+]$	4·02	8·84
$10^3k_1/2{\cdot}303$	3·18	4·63
$10^2k_{\text{La}^{+++}.\text{A}^=}/2{\cdot}303$	5·9	6·0

$10^3[\text{Al}^{+++}]$	3·72	7·36	7·39	7·66
[AcOH]	0·429	0·429	0·427	0·796
[AcONa]	0·353	0·353	0·158	0·354
$10^5[\text{H}^+]$	4·02	4·02	8·94	7·44
$10^3k_1/2{\cdot}303$	23·8	36·5	58·0	43·1
$k_{\text{Al}^{+++}.\text{A}^=}/2{\cdot}303$	6·9	5·6	10·5	6·9

$10^3[\text{Be}^{++}]$	3·84	19·4
[AcOH]	0·429	0·432
[AcONa]	0·350	0·354
$10^5[\text{H}^+]$	4·06	4·03
$10^3k_1/2{\cdot}303$	39·4	118·2
$k_{\text{Be}^{++}.\text{A}^=}/2{\cdot}303$	11·5	7·1

TABLE 4.

M	$0{\cdot}434k_{\text{M}.\text{A}^=}$	M	$0{\cdot}434k_{\text{M}.\text{A}^=}$	M	$0{\cdot}434k_{\text{M}.\text{A}^=}$
H^+	54·8	Cd^{++}	$1{\cdot}4 \times 10^{-2}$	Mg^{++}	$\sim 0{\cdot}5 \times 10^{-2}$
Cu^{++}	15·8	Pb^{++}	$3{\cdot}5 \times 10^{-2}$	$\text{Co(NH}_3)_6{}^{+++}$	~ 0
Ni^{++}	$15{\cdot}4 \times 10^{-2}$	Mn^{++}	$2{\cdot}3 \times 10^{-2}$	Al^{+++}	(7)
Zn^{++}	$9{\cdot}6 \times 10^{-2}$	La^{+++}	$5{\cdot}9 \times 10^{-2}$	Be^{++}	(11)
Co^{++}	$9{\cdot}0 \times 10^{-2}$				

arises here through a subtle though not unreasonable interplay of rate and equilibrium constants. The first-order constant observed is equal to that for the decomposition of acetoacetic acid (cf. the value calculated from Ljunggren's results) and also to $k_1/2$, where, since $k_{A^=}\ \alpha_{A^=}$ is negligible at this pH,

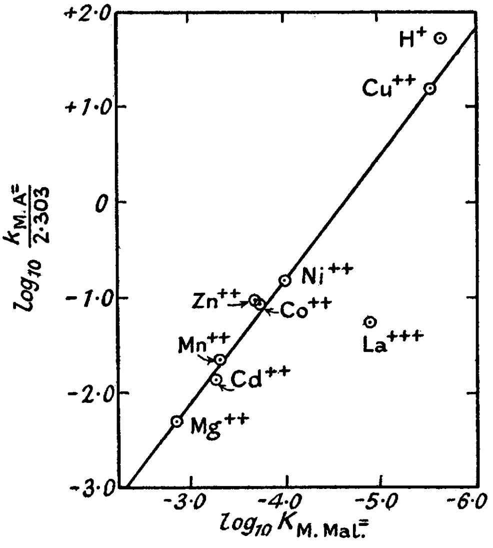
$$k_1 = k_{H_2A}\alpha_{H_2A} + k_{HA^-}\alpha_{HA^-} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (10)$$

with

$$\alpha_{H_2A} + \alpha_{HA^-} + \alpha_{A^=} = 1\ ;\ \alpha_{HA^-}[H^+]/\alpha_{H_2A} = K_1\ ;$$
$$\alpha_{A^=}[H^+]/\alpha_{HA^-} = K_2\ ;\ [H^+] = (\alpha_{HA^-} + 2\alpha_{A^=})m$$

The value of k_{HA^-} being known, a value for k_{H_2A} was obtained from a measurement in 0·1m-hydrochloric acid solution to repress the ionisation of the acetonedicarboxylic acid. The first-order plot is curved (Fig. 3), corresponding to $k_1 < 2k_2$. Application of Swain's method for the analysis of the kinetics of consecutive irreversible unimolecular reactions (*J. Amer. Chem. Soc.*, 1944, **66**, 1696) gives $k_1 = 11·0 \times 10^{-3}$ and $k_2 = 7·9 \times 10^{-3}$, and these values give a theoretical curve which fits the experimental curve well. Thus k_2 is unaffected by addition of acid, whilst k_1 is decreased to a value equal to k_{H_2A}. Wiig (*loc. cit.*) investigated the effect of addition of acid, but did not detect the deviation of the first-order plots from linearity, and ascribed the decrease of rate to the formation of a complex between the acetonedicarboxylic acid and the added hydrochloric acid. Since both acetonedicarboxylic acid and the univalent ion are decarboxylated at not very different rates, the kinetic data are not suitable for obtaining an accurate value of K_1. However, substitution of $k_1 = 15·8 \times 10^{-3}$, $k_{H_2A} = 11·0 \times 10^{-3}$, $k_{HA^-} = 26·5 \times 10^{-3}$, and $m =$ 0·007 (half the initial value) in equations (10) gives $K_1 = 1·4 \times 10^{-3}$, of the same order as the other approximate value calculated from the titration curve at room temperature.

FIG. 4.

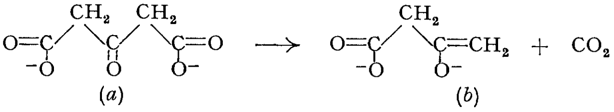


The addition of cupric ions (0·058m) to the unbuffered solution causes the rapid loss of one molecule of carbon dioxide (Fig. 3). The initial slope gives $k_1 = 90 \times 10^{-3}$, and expressing k_1 as

$$k_1 = k_{H_2A}\alpha_{H_2A} + k_{HA^-}\alpha_{HA^-} + k_{Cu^{++}.HA^-}\alpha_{HA^-}[Cu^{++}] + k_{Cu^{++}.A^=}\alpha_{A^=}[Cu^{++}] \quad (11)$$

we get $k_{Cu^{++}.HA^-} \sim 3·0$, a factor of 10 less than $k_{Cu^{++}.A^=}$. The addition of cupric ions to the solution in 0·1m-hydrochloric acid caused no acceleration of the rate.

(c) *General Conclusions.*—A simple bond rearrangement of the bivalent acetonedicarboxylate ion leads to the loss of a molecule of carbon dioxide and the production of an enolate anion :



A similar mechanism has been suggested in the case of αα-dimethylacetoacetic acid to account for the identity of the rates of bromination and decarboxylation (Pedersen, *J. Amer. Chem. Soc.*, 1936, **58**, 240). If the activated complex closely resembles (*b*) it is reasonable that the reaction should be catalysed by hydrogen ions; enols are much weaker acids than carboxylic acids (Schwarzenbach and Lutz, *Helv. Chim. Acta*, 1940, **23**, 1147) and hence an added proton will stabilise (*b*) more than (*a*). In the case of nitroacetic acid (Pedersen, *Trans. Faraday Soc.*, 1927, **23**, 316) the un-ionised acid is stable and only the univalent anion is decarboxylated; this corresponds to the much higher acidic strength of the aci-form of nitro-compounds (Hammett, " Physical Organic Chemistry," p. 250, New York, 1940). The addition of a second proton to the acetonedicarboxylate activated complex appears to " block " one of the carboxylate groups and to reduce the rate to a value close to that for acetoacetic acid ($k_{\mathrm{H_2A}} = 11{\cdot}0 \times 10^{-3}$, $k_2 = 7{\cdot}9 \times 10^{-3}$).

The absence of catalysis by the triply charged hexamminocobaltic ion indicates that the cation catalysis is due to an interaction of a specific short-range character between cation and activated complex. If the activated complex does indeed resemble (*b*), it might be expected readily to form complexes of the chelate type; its complexing powers should be similar to those of the bivalent malonate ion. The beryllium ion with a high catalytic coefficient forms a complex of considerable stability with the malonate ion, beryllium malonate solutions having an abnormally low conductivity (Sidgwick and Lewis, *J.*, 1926, 1287, 2538). Davies and Stock (*J.*, 1949, 1371) give values for the dissociation constants of the complexes formed by the bivalent malonate anion with a number of bivalent metal ions at 18°, and Peacock and James (*J.*, 1951, 2233) have provided additional data for the lanthanum and hexamminocobaltic ions. Fig. 4 is a plot of the logarithm of these values against the logarithm of the corresponding catalytic coefficients obtained in this work; there is a linear free-energy relationship between the related rate and equilibrium data for the bivalent ions. For a number of ligands the order $\mathrm{Mn^{++}} < \mathrm{Co^{++}} < \mathrm{Ni^{++}} < \mathrm{Cu^{++}} > \mathrm{Zn^{++}}$ is found for the stabilities of the complexes formed (Irving and Williams, *Nature*, 1948, **162**, 746). Such parallelisms further substantiate the postulate made concerning the nature of the activated complex; it is in cases such as this where the activated complex can chelate with metal ions that marked catalytic effects may be expected. Pedersen (*Acta Chem. Scand.*, 1948, **2**, 385) has lately investigated the cation-catalysed halogenation of a β-keto-ester. He considers it necessary to postulate some complex formation between the keto-ester and the cation, but it seems likely that the more important interaction is a chelation between activated complex and cation.

The effects of the cations vary from the large catalytic effect observed with, *e.g.*, cupric ions, to much smaller effects which might be classified as specific primary kinetic salt effects. However, specific effects arise from the short-range interactions between pairs of ions of opposite charge (Brönsted, *J. Amer. Chem. Soc.*, 1922, **44**, 877), and a short-range attractive interaction of an ion with the activated complex is clearly equivalent to the chelation postulated here and will lead to a term involving the concentration of this ion in the rate equation.

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