410. *Acid–Base Catalysis in the Depolymerisation of Dimeric Dihydroxyacetone.*

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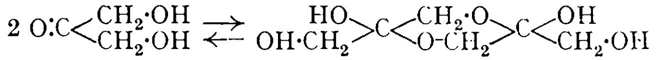
The depolymerisation of dimeric dihydroxyacetone in aqueous solution has been studied kinetically by a dilatometric method. The reaction is of the first order, and is catalysed by both acids and bases in general. By using suitable buffer solutions catalytic constants were evaluated for H_2O, H_3O^+, OH^-, four carboxylic acids, and seven carboxylate ions. For both acid and basic catalysis there is a relation between the catalytic constants and the acid or basic strength of the catalysts. It cannot be decided whether the catalysis by water molecules represents acid or basic catalysis, or both.

It has long been known that a number of α-hydroxy-aldehydes and -ketones have twice the expected molecular weight in freshly prepared solutions, but change slowly to the unimolecular form on keeping. This behaviour has been observed with glycollaldehyde (Fenton and Jackson, J., 1899, **75**, 575), glyceraldehyde (Wohl, *Ber.*, 1898, **31**, 2394), and dihydroxyacetone (Bertrand, *Compt. rend.*, 1899, **129**, 341), and experiments in this laboratory with phenylglyceraldehyde, prepared by Fischer's method (*Ber.*, 1898, **31**, 1995), have shown that this substance behaves in the same manner. Little work has been done on the kinetics of the depolymerisation, though Bertrand's data (*loc. cit.*) suggest that the reaction is of the first order for dihydroxyacetone in water, and the same conclusion was reached by McCleland (J., 1911, **99**, 1827) for glycollaldehyde in a number of solvents.

The existence of dimeric forms is almost certainly due to semi-acetal formation between the two molecules, *e.g.*, for dihydroxyacetone :



$$2\,\mathrm{O{:}C}{<}\begin{matrix}\mathrm{CH_2{\cdot}OH}\\ \mathrm{CH_2{\cdot}OH}\end{matrix} \rightleftarrows \begin{matrix}\mathrm{HO}\\ \mathrm{OH{\cdot}CH_2}\end{matrix}{>}\mathrm{C}{<}\begin{matrix}\mathrm{CH_2{\cdot}O}\\ \mathrm{O{\cdot}CH_2}\end{matrix}{>}\mathrm{C}{<}\begin{matrix}\mathrm{OH}\\ \mathrm{CH_2{\cdot}OH}\end{matrix} \quad . \quad . \quad . \quad (1)$$

In the pentoses and hexoses an exactly similar linking between carbonyl and hydroxyl groups in the *same* molecule leads to the formation of a pyranose ring. The rupture of these pyranose rings is responsible for the phenomenon of mutarotation, the kinetics of which constitute one of the most interesting examples of general acid–base catalysis (cf. Brönsted and Guggenheim, *J. Amer. Chem. Soc.*, 1927, **49**, 2554; Lowry and Smith, J., 1927, 2539), and we might expect by analogy that the same kind of behaviour would be exhibited by the depolymerisation of the dimeric forms described above. The present paper describes a study of the depolymerisation kinetics in aqueous solutions of dihydroxyacetone, which is the most accessible of the substances mentioned.

EXPERIMENTAL.

Materials.—The dihydroxyacetone was a commercial product known as " oxantin," m. p. 77—84°, depending on the rate of heating. Previous values for the m. p. of the pure substance are 74—75° (Virtanen and Nordlund, *Biochem. J.*, 1933, **27**, 442), about 80° (Bertrand, *Ann. Chim. Phys.*, 1904, **3**, 253), and 68—75° (Piloty, *Ber.*, 1897, **30**, 3165), and it is probable that the indefinite m. p. is due to partial depolymerisation on melting. Treatment with a slight excess of 2 : 4-dinitrophenylhydrazine in 2N-hydrochloric acid gave an almost quantitative yield of hydrazone, m. p. 160°, raised to 161° by recrystallising twice from 50% methyl alcohol. Collatz and Neuberg (*Biochem. Z.*, 1930, **223**, 494) give 163° for the pure derivative. Finally, the oxantin did not react with bromine under the conditions given by Collatz and Neuberg (*loc. cit.*), and was therefore free from glyceraldehyde and similar substances. It thus appears to be fairly pure dihydroxyacetone, and since recrystallisation from acetone was very wasteful, it was used without further purification. It gave a neutral solution in water.

The acids used were mostly pure commercial products. Chloroacetic acid was purified by recrystallisation from benzene, and acrylic acid by fractional freezing. Trimethylacetic acid was prepared from pinacol and fractionated in a vacuum. The purity of the solid acids was checked by titration, values better than 99% of the theoretical being obtained in each case.

All solutions were made with water freed from carbon dioxide, and the acid solutions were standardised directly against the sodium hydroxide solution used for making up the buffer solutions.

Measurement of Reaction Velocity.—It might be expected that the reaction shown in equation (1) would be accompanied by a considerable volume change, and it was in fact found that in aqueous solution the reaction from right to left results in an expansion of about 36 cu. mm. per g. of dihydroxyacetone. The reaction could thus be followed conveniently by a dilatometric method. Two dilatometers were used having severally volumes of 31 and 20 c.c. and capillaries of cross-section 0·233 and 0·105 sq. mm. The solutions used contained about 1% of dihydroxyacetone by weight, and the total movement obtained in the two capillaries was about 60 mm. and 100 mm. respectively. The experiments were carried out in a thermostat at $25° \pm 0·005°$, and the height of the meniscus could be read to the nearest 0·1 mm.

Dissolution of dihydroxyacetone in water is accompanied by a considerable heat absorption, and it is necessary to allow time for the solution to regain thermostat temperature before reliable readings can be obtained. In acid solutions of concentration about $4—8 \times 10^{-4}$ the depolymerisation is very slow (see below), and this fact was utilised in devising a method to enable fast reactions to be studied. 0·3—0·4 G. of dihydroxyacetone was dissolved in 10 c.c. of 6×10^{-4}N-hydrochloric acid at 25°, and the solution kept in the thermostat for 20 minutes. 25 C.c. of the catalysing solution (previously de-aerated and brought to thermostat temperature) were then added, and the mixed solution immediately transferred to the dilatometer. It was thus possible to obtain reliable readings 4—5 minutes after mixing. The acid present was allowed for in calculating the actual composition.

The course of the reaction was found to be strictly of the first order, and the velocity constants were calculated by Guggenheim's method (*Phil. Mag.*, 1926, **2**, 540), 30—60 readings being taken in each set. Table I gives the details of a typical experiment, the calculated values of Δx being given by the equation $\log_{10} \Delta x = 1·705 - 0·00812t$, where t is the time in minutes. In all the first-order velocity constants given, the time is measured in minutes and decadic logarithms are used. Concentrations are in g.-mols. per 1000 g. of solution.

TABLE I.

0·128N-*Mandelic acid* + 0·0980N-*sodium mandelate.*

Δt = 100 minutes.

(Only alternate readings are recorded.)

	Δx (mm.).		Diff.		Δx (mm.).		Diff.		Δx (mm.).		Diff.
t.	Obs.	Calc.	(mm.).	t.	Obs.	Calc.	(mm.).	t.	Obs.	Calc.	(mm.).
10	41·8	42·1	− 0·3	42	23·2	23·1	+ 0·1	74	12·5	12·7	− 0·2
14	38·9	39·0	− 0·1	46	21·5	21·5	0·0	78	11·8	11·8	0·0
18	36·2	36·2	0·0	50	20·0	19·9	+ 0·1	82	10·9	10·9	0·0
22	33·5	33·6	− 0·1	54	18·4	18·5	− 0·1	86	10·1	10·1	0·0
26	31·1	31·2	− 0·1	58	17·1	17·1	0·0	90	9·6	9·3	+ 0·3
30	28·9	28·9	0·0	62	15·9	15·9	0·0	94	8·7	8·8	− 0·1
34	27·0	26·9	+ 0·1	66	14·9	14·8	+ 0·1	98	8·0	8·1	− 0·1
38	25·0	24·9	+ 0·1	70	13·7	13·7	0·0	100	7·7	7·7	0·0

In some cases when the solutions were allowed to remain in the dilatometer for several days, a very slow contraction was observed : this is probably due to the irreversible polymerisation of the dihydroxyacetone to higher sugars. This change was much too slow to interfere with the depolymerisation kinetics.

Results.

Hydrochloric Acid Solutions.—In the mutarotation of glucose there is a considerable range of hydrogen-ion concentrations over which catalysis by both hydrogen and hydroxyl ions can be neglected. Preliminary experiments with hydrochloric acid solutions of different concentrations showed that this is not the case with the present reaction, since the velocity passes through a fairly sharp minimum at about 6×10^{-4}N., rising very rapidly on the alkaline side of the minimum. Acid solutions more dilute than about 10^{-3}N. did not give completely reproducible results (presumably because of the large effect of small quantities of impurities), and Table II contains only results for higher concentrations than this, *i.e.*, well on the acid side of the minimum.

TABLE II.

$[HCl] \times 10^4$	292	243	213	184	150	107	86·0	52·4	23·2
10^4k obs.	479	417	373	337	295	224	203	131	77·6
10^4k calc.	527	443	391	342	284	210	174	116	65·4

The relation between velocity constant and acid concentration is approximately linear, and when these are plotted there is a finite intercept at $[H_3O^+] = 0$. The value of this intercept is not given accurately by this set of experiments, but certainly lies between $k \times 10^4 = 20$ and 40. If we use the value $10^4k_0 = 25{\cdot}5$ derived later for the water catalysis, the results are best expressed by

$$k = 0{\cdot}00255 + 1{\cdot}72[H_3O^+] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

giving 1·72 as the mean value of the catalytic constant of the ion H_3O^+. The rates calculated from equation (2) are given in the third row of Table II. There is clearly a slight drift in catalytic constant with concentration, probably due to a primary salt effect, though the addition of 0·2M-sodium chloride has no appreciable effect on the velocity. (For a reaction involving an ion and a neutral molecule a specific salt effect is to be anticipated.)

Buffer Solutions.—In a buffer solution containing an uncharged acid A and the corresponding base B (*i.e.*, the anion of the acid) the general expression for the reaction velocity is

$$k = k_0 + k_{H_3O^+}[H_3O^+] + k_{OH^-}[OH^-] + k_A[A] + k_B[B] \quad . \quad . \quad . \quad . \quad (3)$$

where k_0 is the velocity of the water-catalysed reaction, and k_X is the catalytic constant of the species X. Equation (3) can be rewritten in the form

$$k = k' + \alpha[B] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where $k' = k_0 + k_{H_3O^+}[H_3O^+] + k_{OH^-}[OH^-]$
and $\alpha = k_B + k_A[A]/[B]$

As stated above, there are no conditions under which it is possible to neglect the last two terms in k', and in order to derive values for the separate catalytic constants it is necessary to carry out series of experiments in which $[H_3O^+]$ and $[OH^-]$ are constant. This was effected by varying [A] and [B] but keeping the ratio [A]/[B] constant, and also keeping the total salt concentration constant at 0·1N. by adding sodium chloride when necessary. Under these conditions k' and α are constant for a given series and can be obtained graphically from the linear plot of k against [B]. Finally, by carrying out two or more such series with different values of [A]/[B], the separate values of k_B and k_A can be obtained. On account of the very

TABLE III.

Trimethylacetic acid; $k_B = 4{\cdot}2 \times 10^{-1}$.

$[A]/[B] = 1{\cdot}034$, $[H_3O^+] = 1{\cdot}52 \times 10^{-5}$, $10^4k' = 456$.

$[CMe_3{\cdot}COO^-]$ …………	0·0501	0·0398	0·0300	0·0225	0·0100
10^4k obs. …………	644	639	582	540	499
10^4k calc. …………	666	623	582	551	498

$[A]/[B] = 1{\cdot}795$, $[H_3O^+] = 2{\cdot}64 \times 10^{-5}$, $10^4k' = 276$.

$[CMe_3{\cdot}COO^-]$ …………	0·0305	0·0229	0·0151	0·00726
10^4k obs. …………	401	372	338	308
10^4k calc. …………	404	372	340	307

Acetic acid; $k_B = 1{\cdot}60 \times 10^{-1}$.

$[A]/[B] = 0{\cdot}980$, $[H_3O^+] = 2{\cdot}69 \times 10^{-5}$, $10^4k' = 266$.

$[CH_3{\cdot}COO^-]$ …………	0·1004	0·0505	0·0316	0·0129
10^4k obs. …………	424	350	318	284
10^4k calc. …………	427	347	317	287

$[A]/[B] = 1{\cdot}304$, $[H_3O^+] = 3{\cdot}56 \times 10^{-5}$, $10^4k' = 217$.

$[CH_3{\cdot}COO^-]$ …………	0·1045	0·0785	0·0533	0·0204
10^4k obs. …………	380	335	294	254
10^4k calc. …………	384	342	302	249

$[A]/[B] = 3{\cdot}38$, $[H_3O^+] = 9{\cdot}27 \times 10^{-5}$, $10^4k' = 96{\cdot}0$.

$[CH_3{\cdot}COO^-]$ …………	0·1027	0·0750	0·0409	0·0127
10^4k obs. …………	260	218	167	124
10^4k calc. …………	260	216	162	116

$[A]/[B] = 4{\cdot}83$, $[H_3O^+] = 1{\cdot}32 \times 10^{-4}$, $10^4k' = 74{\cdot}0$.

$[CH_3{\cdot}COO^-]$ …………	0·1026	0·0871	0·0683	0·0512	0·0303	0·0103
10^4k obs. …………	234	218	178	157	125	92·6
10^4k calc. …………	238	213	183	156	123	90·4

TABLE III (*continued*).

Phenylacetic acid; $k_B = 1{\cdot}22 \times 10^{-1}$.

$[A]/[B] = 0{\cdot}700$, $[H_3O^+] = 5{\cdot}32 \times 10^{-5}$, $10^4k' = 142$.

$[CH_2Ph{\cdot}COO^-]$	0·1036	0·0775	0·0514	0·0263
10^4k obs.	270	234	209	170
10^4k calc.	268	237	205	174

Acrylic acid; $k_B = 1{\cdot}15 \times 10^{-1}$.

$[A]/[B] = 0{\cdot}500$, $[H_3O^+] = 4{\cdot}34 \times 10^{-5}$, $10^4k' = 181$.

$[CH_2{:}CH{\cdot}COO^-]$	0·102	0·0668	0·0334
10^4k obs.	291	255	226
10^4k calc.	298	258	220

$[A]/[B] = 2{\cdot}50$, $[H_3O^+] = 2{\cdot}17 \times 10^{-4}$, $10^4k' = 60{\cdot}7$.

$[CH_2{:}CH{\cdot}COO^-]$	0·101	0·0667	0·0333
10^4k obs.	177	142	98·0
10^4k calc.	177	137	99·0

Formic acid; $k_A = 5{\cdot}4 \times 10^{-3}$; $k_B = 3{\cdot}21 \times 10^{-2}$.

$[A]/[B] = 0{\cdot}493$, $[H_3O^+] = 1{\cdot}36 \times 10^{-4}$, $10^4k' = 84{\cdot}0$.

$[H{\cdot}COO^-]$	0·1016	0·0710	0·0506	0·0205
10^4k obs.	119·5	108·7	101·2	91·2
10^4k calc.	119·3	108·7	101·6	91·1

$[A]/[B] = 1{\cdot}54$, $[H_3O^+] = 4{\cdot}26 \times 10^{-4}$, $10^4k' = 49{\cdot}1$.

$[H{\cdot}COO^-]$	0·0993	0·0743	0·0497	0·0245
10^4k obs.	90·1	79·0	69·6	59·0
10^4k calc.	89·3	79·1	69·2	59·0

$[A]/[B] = 3{\cdot}66$, $[H_3O^+] = 1{\cdot}01 \times 10^{-3}$, $10^4k' = 56{\cdot}2$.

$[H{\cdot}COO^-]$	0·1007	0·0760	0·0503	0·0247
10^4k obs.	108·3	95·4	82·2	71·4
10^4k calc.	108·9	95·6	82·2	68·9

Mandelic acid; $k_A = 1{\cdot}04 \times 10^{-2}$; $k_B = 2{\cdot}00 \times 10^{-2}$.

$[A]/[B] = 0{\cdot}129$, $[H_3O^+] = 7{\cdot}78 \times 10^{-5}$, $10^4k' = 106{\cdot}2$.

$[CHPh(OH){\cdot}COO^-]$ ...	0·100	0·0750	0·0500	0·0250
10^4k obs.	130·3	122·0	120·2	110·6
10^4k calc.	127·5	122·2	116·9	111·6

$[A]/[B] = 0{\cdot}613$, $[H_3O^+] = 3{\cdot}70 \times 10^{-4}$, $10^4k' = 46{\cdot}7$.

$[CHPh(OH){\cdot}COO^-]$ ...	0·0996	0·0747	0·0498	0·0249
10^4k obs.	73·4	66·3	61·4	52·5
10^4k calc.	73·0	66·4	59·8	53·3

$[A]/[B] = 1{\cdot}30$, $[H_3O^+] = 7{\cdot}82 \times 10^{-4}$, $10^4k' = 46{\cdot}1$.

$[CHPh(OH){\cdot}COO^-]$ ...	0·0980	0·0735	0·0490	0·0245
10^4k obs.	81·2	70·6	62·0	55·6
10^4k calc.	78·9	70·7	62·5	54·6

Chloroacetic acid; $k_A = 1{\cdot}62 \times 10^{-2}$; $k_B = 6{\cdot}0 \times 10^{-3}$.

$[A]/[B] = 0{\cdot}200$, $10^4k' = 45{\cdot}3$.

$[CH_2Cl{\cdot}COO^-]$	0·1005	0·0753	0·0502	0·0251
$[H_3O^+] \times 10^4$	4·23	4·19	4·13	3·93
10^4k obs.	54·0	53·6	52·0	48·3
10^4k corr.	53·8	53·4	51·6	47·5
10^4k calc.	54·5	52·2	49·9	47·6

$[A]/[B] = 0{\cdot}800$, $10^4k' = 63{\cdot}3$.

$CH_2Cl{\cdot}COO^-]$	0·0994	0·0745	0·0497	0·0248
$[H_3O^+] \times 10^3$	1·69	1·67	1·64	1·55
10^4k obs.	82·2	79·6	72·4	65·4
10^4k corr.	82·8	80·5	73·9	68·4
10^4k calc.	82·0	77·4	72·7	68·0

$[A]/[B] = 1{\cdot}40$, $10^4k' = 90{\cdot}1$.

$[CH_2Cl{\cdot}COO^-]$	0·0937	0·0703	0·0468	0·0234
$[H_3O^+] \times 10^3$	2·93	2·89	2·83	2·64
10^4k obs.	114·4	108·4	99·2	89·8
10^4k corr.	116·1	110·9	102·8	97·0
10^4k calc.	117·0	110·3	103·5	96·8

TABLE III (*continued*).

Cyanoacetic acid; $k_A = 3{\cdot}2 \times 10^{-2}$.

$[CH_2(CN){\cdot}CO_2H]$.	$[CH_2(CN){\cdot}COO^-]$.	$[H_3O^+] \times 10^4$.	10^4k		
			Obs.	Corr.	Calc.
0·0498	0·0996	26·4	92·8	40·4	41·5
0·0374	0·0747	25·9	88·2	36·8	37·5
0·0299	0·0996	15·9	68·2	35·2	35·1
0·0224	0·0747	15·6	65·2	33·5	32·7
0·0149	0·0498	15·3	61·0	31·2	30·3
0·0102	0·102	5·38	51·9	29·4	28·8
0·00752	0·0752	5·31	49·5	27·0	27·9

great catalytic effect of the hydroxyl ion, it was necessary in most cases to keep the hydrogen-ion concentration greater than about 10^{-4}: this restricted the choice of acids to those readily soluble in water.

The results for buffer solutions are given in Table III. For trimethylacetic, acetic, phenylacetic, acrylic, formic, and mandelic acids the results were treated as described above, and the values of k_A and k_B obtained are given at the head of each section. The calculated values of k were obtained by inserting these values of k_A and k_B and the observed values of k' in equation (4). In the case of trimethylacetic, acetic, and acrylic acids no acid catalysis could be detected, the value of α being sensibly the same for different values of [A]/[B]. On account of the limited solubility of phenylacetic acid it was not feasible to vary [A]/[B] over any considerable range, but we may assume that catalysis by undissociated acid can also be neglected in this case.

With chloroacetic acid it is necessary to allow for the fact that the actual value of [A]/[B] differs appreciably from the stoicheiometric ratio and changes slightly when the buffer is diluted. The hydrogen-ion concentration is therefore not quite constant in each series, the actual values being given in the table. The values of k (corr.) represent the velocity constants which would be obtained if [A]/[B] were constant and equal to the stoicheiometric ratio in each series: in applying the correction only the values of $k_{H_3O^+}$ and k_{OH^-} are needed, since the variations in the catalytic effect of the other species are negligible. The corrected values are then treated as described above. The methods of calculating $[H_3O^+]$, $[OH^-]$, and k_{OH^-} are given below.

These corrections are negligible for the weaker acids studied, but they are still larger for the stronger cyanoacetic acid, and it is not possible to obtain a reliable value for the small catalytic effect of the cyanoacetate ion. The values of k (corr.) in the table were obtained by subtracting from the observed velocity the calculated velocities due to the ions H_3O^+ and OH^-, and the calculated velocity constants are given by

$$k = 0{\cdot}00255 + k_A[A] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

the catalysis by $CH_2(CN){\cdot}COO^-$ being assumed to be negligible.

The values of k' correspond to catalysis by H_2O, OH^-, and H_3O^+, and it is clear from the results in acid solutions that the last of these three can be neglected when $[H_3O^+] <$ *ca.* 10^{-4}. The values of k' for buffers in this range can therefore be used to obtain values of k_{OH^-} and k_0. The concentrations of hydrogen and hydroxyl ions in these buffers are given by the equations

$$[H_3O^+] = f_A[A]K_A/f_Bf_{H_3O^+}[B]; \qquad [OH^-] = K_w'/[H_3O^+] \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where K_w' is the ionic product of water at an ionic strength of 0·1 and K_A is the thermodynamic dissociation constant of the acid. In most cases [A]/[B] can be taken as the stoicheiometric buffer ratio, but for chloro- and cyano-acetic acids the mass-action equation must be solved. Harned and Hamer (*J. Amer. Chem. Soc.*, 1933, **55**, 2198) give $1{\cdot}61 \times 10^{-14}$ for K_w' in 0·1N-sodium chloride at 25°, and this value has been used throughout. Larsson and Adell (*Z. physikal. Chem.*, 1931, **156**, *A*, 352, 381) have measured the value of $f_Bf_{H_3O^+}/f_A$ for ten carboxylic acids in 0·1N-sodium chloride, and find values which are all within a few units % of 0·641: this value has therefore been used in calculating all the hydrogen- and hydroxyl-ion concentrations. (The previous treatment has been based on the assumption that the activity coefficients depend only on the total concentration of uni-univalent salt, and not on the nature of the other ions present: hence there is no point in attempting to distinguish between values in NaCl and in NaB.) The calculated values of $[H_3O^+]$ are given in Table III, and Table IV contains the values of $[H_3O^+]$, $[OH^-]$, and k' for buffers of $p_H > 4$. The values of K_A used, together with their sources, are given in Table V. The results are well represented by the equation

$$k' = 0{\cdot}00255 + 4{\cdot}03 \times 10^7[OH^-] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

which is the basis of the calculated values in the table. This gives an accurate value for k_{OH^-}, and a value for k_0 which is consistent with the results in hydrochloric acid solutions and in cyanoacetate buffers.

TABLE IV.

Acid.	[A]/[B].	$[H_3O^+] \times 10^5$.	$[OH^-] \times 10^{10}$.	$10^4k'$.	
				Obs.	Calc.
Trimethylacetic	1·034	1·52	10·64	456	455
,,	1·795	2·64	6·12	276	273
Acetic	0·980	2·69	6·00	266	268
,,	1·304	3·56	4·53	217	210
,,	3·38	9·27	1·74	96·0	96·2
Phenylacetic	0·700	5·32	3·04	142	148
Acrylic	0·500	4·34	3·73	181	176
Mandelic	0·129	7·78	2·08	106	110

For the other buffer solutions both hydrogen- and hydroxyl-ion catalysis contribute to k'. The observed values show good general agreement (to within 10%) with the equation

$$k' = 0{\cdot}00255 + 1{\cdot}72[H_3O^+] + 4{\cdot}03 \times 10^7[OH^-] \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

[cf. equations (2) and (7)]: this is as close as can be expected in view of the simplifying assumptions made about the activity coefficients. The value of k' passes through a minimum at about $[H_3O^+] = 6 \times 10^{-4}$, where its value is about 0·0046, *i.e.*, nearly twice the "spontaneous" rate k_0 due to catalysis by water molecules. It may be noted that the value derived for k_{OH^-} depends on the figure chosen for the activity coefficient factor in equation (6), while the other catalytic constants are independent of this choice.

DISCUSSION OF RESULTS.

The above results show that the depolymerisation of dimeric dihydroxyacetone is subject to general catalysis by both acids and bases, like the analogous mutarotation reaction. Table V gives the catalytic constants of the different species studied, together with the acid dissociation constants K_A. The figure shows a plot of $\log_{10} k_A$ and $\log_{10} k_B$ against $\log_{10} K_A$ for the carboxylic acids and their anions.

TABLE V.

Acid.	Base.	k_A.	k_B.	K_A.
H_2O	OH^-	$(4{\cdot}6 \times 10^{-5})$	$3{\cdot}03 \times 10^{-7}$	$1{\cdot}79 \times 10^{-16}$
$CMe_3\cdot CO_2H$	$CMe_3\cdot COO^-$	—	$4{\cdot}20 \times 10^{-1}$	$9{\cdot}40 \times 10^{-6}$ (*a*)
$CH_3\cdot CO_2H$	$CH_3\cdot COO^-$	—	$1{\cdot}60 \times 10^{-1}$	$1{\cdot}75 \times 10^{-5}$ (*b*)
$CH_2Ph\cdot CO_2H$	$CH_2Ph\cdot COO^-$	—	$1{\cdot}22 \times 10^{-1}$	$4{\cdot}88 \times 10^{-5}$ (*c*)
$CH_2\colon CH\cdot CO_2H$	$CH_2\colon CH\cdot COO^-$	—	$1{\cdot}15 \times 10^{-1}$	$5{\cdot}56 \times 10^{-5}$ (*d*)
$H\cdot CO_2H$	$H\cdot COO^-$	$5{\cdot}4 \times 10^{-3}$	$3{\cdot}21 \times 10^{-2}$	$1{\cdot}77 \times 10^{-4}$ (*e*)
$CHPh(OH)\cdot CO_2H$	$CHPh(OH)\cdot COO^-$	$1{\cdot}04 \times 10^{-2}$	$2{\cdot}00 \times 10^{-2}$	$3{\cdot}86 \times 10^{-4}$ (*f*)
$CH_2Cl\cdot CO_2H$	$CH_2Cl\cdot COO^-$	$1{\cdot}62 \times 10^{-2}$	$6{\cdot}0 \times 10^{-3}$	$1{\cdot}38 \times 10^{-3}$ (*g*)
$CH_2(CN)\cdot CO_2H$	$CH_2(CN)\cdot COO^-$	$3{\cdot}2 \times 10^{-2}$	—	$3{\cdot}56 \times 10^{-3}$ (*h*)
H_3O^+	H_2O	1·72	$(4{\cdot}6 \times 10^{-5})$	$5{\cdot}55 \times 10$

(*a*) Larsson and Adell, *loc. cit.*, p. 352; (*b*) Harned and Ehlers, *J. Amer. Chem. Soc.*, 1933, **55**, 652; (*c*) Jeffery and Vogel, J., 1934, 166; (*d*) Dippy and Lewis, this vol., p. 1008; (*e*) Harned and Embree, *J. Amer. Chem. Soc.*, 1934, **56**, 1042; (*f*) Davies, private communication; (*g*) Wright, *J. Amer. Chem. Soc.*, 1934, **56**, 314; (*h*) Davies, *Phil. Mag.*, 1927, **4**, 244.

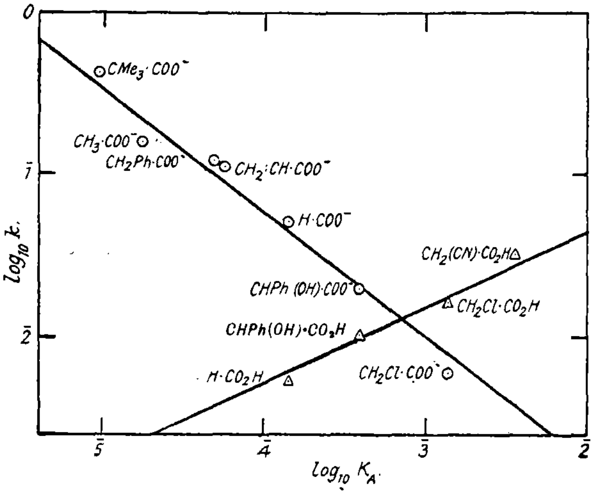
The straight lines in the figure represent the equations

$$k_A = 0{\cdot}20K_A^{0{\cdot}38} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and

$$k_B = 5{\cdot}0 \times 10^{-5}(1/K_A)^{0{\cdot}76} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

the exact values of the constants having been chosen so as to agree with the results for the ions H_3O^+ and OH^- respectively. The figure shows that this choice of constants agrees well with the results for anion catalysis, and is consistent with the somewhat meagre data for catalysis by acid molecules. The Brönsted equation thus appears to be obeyed over ranges of 13 and 5 powers of ten for basic and acid catalysis respectively.



The values predicted by equations (9) and (10) for trimethylacetic, acetic, and acrylic acids and the cyanoacetate ion are consistent with the failure to detect catalysis by these species under the conditions of experiment.

The catalytic constant for water molecules was obtained by dividing the "spontaneous" rate k_0 by 55·5, and its interpretation offers a special point of interest. The only other reactions in which general catalysis by both acids and bases has been studied are the mutarotation of glucose (Brönsted and Guggenheim, *loc. cit.*) and the acetone–iodine reaction (Dawson *et al.*, J., 1926—1936), and in both cases it is clear from the results with other catalysts that the acid catalysis by water molecules is negligible compared with the basic catalysis. In the present case, however, the values of k_A and k_B calculated from equations (9) and (10) are of the same order of magnitude, so that we cannot exclude the possibility that both types of catalysis contribute to the observed "spontaneous" rate, especially as the observed value of $k_0/55{\cdot}5$ is considerably greater than the calculated value of either k_A or k_B.

The exponent of the Brönsted equation has the value 0·38 for acid catalysis, which is not far different from the value 0·3 found for the mutarotation of glucose. For basic catalysis, on the other hand, the exponents for the two reactions are 0·76 and 0·34 respectively: this large difference may be related to the fact that the dihydroxyacetone ring contains two oxygen atoms, whereas the glucose ring contains only one. It is interesting to note that the velocity is throughout proportional to the first power of the catalyst concentration, in spite of the fact that the depolymerisation involves the fission of the ring at two points. In the depolymerisation of paraldehyde (involving the fission of a similar ring at three points) the catalyst concentration appears to enter to a power higher than the first (cf. Bell, Lidwell, and Vaughan-Jackson, J., 1936, 1792).

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