363. *Acid–Base Catalysis in the Depolymerisation of Dimeric Glycollaldehyde.*

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A new form of micro-dilatometer is described which operates with about 1 c.c. of liquid and is suitable for volume changes of 0·2 cu. mm. It has been used to study the kinetics of the depolymerisation of dimeric glycollaldehyde. The reaction is catalysed by both acids and bases, and in general resembles the corresponding reaction for dihydroxyacetone.

It has been shown by Bell and Baughan (J., 1937, 1947) that the conversion of the dimeric form of dihydroxyacetone into the monomeric form is catalysed both by acids and by bases, its general behaviour being similar to that of the mutarotation of glucose. The present paper deals with the analogous reaction for the simplest hydroxy-aldehyde, the change being

$$O\!<\!\begin{matrix}CH(OH)\cdot CH_2\\ CH_2\cdot CH(OH)\end{matrix}\!>\!O \longrightarrow 2CH_2(OH)\cdot CHO$$

Earlier work has shown that the ordinary solid form of glycollaldehyde is the dimer (Fenton and Jackson, J., 1899, **75**, 575) but that on dissolving in water it passes gradually into the monomeric form, this change being kinetically of the first order (McCleland, J., 1911, **99**, 1827). The present investigation of catalytic behaviour showed that it was very similar to that of the more accessible dihydroxyacetone, and the reaction was therefore not studied in great detail. The new form of micro-dilatometer described may, however, be of service in other connexions.

Experimental.

Materials.—Glycollaldehyde was prepared by decarboxylation of dihydroxymaleic acid (cf. Fischer and Taube, *Ber.*, 1927, **60**, 1704). 40 G. of dehydrated acid were warmed at 30° with 100 g. of dry pyridine until frothing had ceased. The bulk of the pyridine was distilled off at 25—30°/8 mm. The temperature was then gradually raised to 150°, the pressure being maintained at 8 mm. and the receiver immersed in a freezing mixture. About 20 c.c. of liquid distilled over, and were freed from pyridine and water by being kept in a vacuum desiccator over sulphuric acid. After 3 weeks the product had solidified to a mass of white crystals, which were washed with ether and dried in air; yield 3·1 g., m. p. 87°, m. p. of 2 : 4-dinitrophenylhydrazone 145°. Collatz and Neuberg (*Biochem. Z.*, 1932, **155**, 27) give m. p. values between 76° and 96° for the aldehyde and 146—151° for the derivative. The product was free from the smell of pyridine and gave a neutral solution in water.

The buffer solutions were prepared as for the measurements with dihydroxyacetone (Bell and Baughan, *loc. cit.*), and the total salt concentration in the reaction mixtures was adjusted to N/10 by the addition of sodium chloride when necessary.

Measurement of Reaction Velocity.—The depolymerisation was again followed by a dilatometric method, but on account of the difficulty and expense of preparing glycollaldehyde it was necessary to devise a method which could be used with about 1 c.c. of solution and 0·02 g. of substance. An ordinary dilatometer of this size would have to have a capillary of about 0·005 sq. mm. cross-section, and would be prohibitively difficult to fill and clean. In the type adopted here (Fig. 1) the capillary is about 1 mm. in internal diameter except at the points *A* and *B*, where it is constricted to about 0·05 mm. The tip *A* is closed during an experiment, and a change of volume therefore causes movement of the meniscus at *B*. However, instead of observing this movement the meniscus is returned to a fixed point by deforming the bulb *C*, and the extent of the deformation necessary serves as a measure of the volume change. The upper part of the limb *D* is attached firmly to a metal plate, and the bulb deformed by lateral motion of the other limb: this is produced and measured by a micrometer screw motion mounted on the same metal plate and attached to *E* by a short silk thread. The fixed point for the meniscus at *B* is the cross-wires of a microscope focused on the capillary.

The sensitivity of the apparatus depends, of course, largely on the shape and thickness of the bulb. In the present work a bulb was used which gave a volume change of about 0·2 cu. mm. for a movement of 1 mm. (measurable to 0·001 mm.) at *E*. Since a temperature change of 0·01° corresponds to a volume change of 0·004 cu. mm., it is clear that the thermostat regulation

is the most important factor in determining the experimental accuracy. The part of the dilatometer outside the thermostat was kept at an approximately constant temperature by the jacket *F* through which was circulated a current of air at thermostat temperature. The relation between the movement of *E* and the volume change was determined by filling the dilatometer with pure water and slowly varying the temperature of the thermostat. Fig. 2 gives a plot of the micrometer scale reading against the specific volume of water at the temperature in question. It will be seen that the relation is linear within the experimental error, so the micrometer readings can be used directly for determining first-order velocity constants.

FIG. 1.

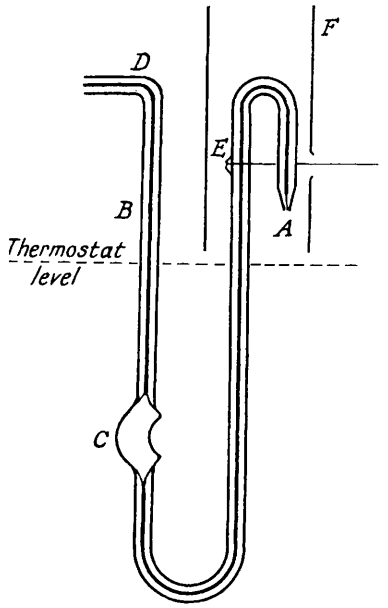
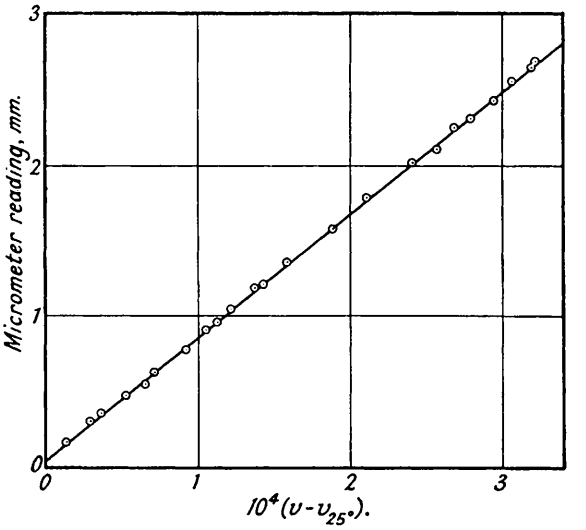


FIG. 2.



A freshly prepared solution of glycollaldehyde underwent first a small expansion, followed by a much larger contraction, the latter being about 20 cu. mm. per g. of aldehyde. Two consecutive stages had also been observed in the depolymerisation of dihydroxyacetone (Bell and Baughan, *loc. cit.*), and the preliminary expansion was in this case attributed to the attainment of temperature equilibrium following heat absorption on dissolving the solid. Experiment showed that this explanation was not feasible for glycollaldehyde, and it is probable that in both cases two consecutive chemical reactions are involved, possibly owing to the double fission of the ring, *e.g.*,

$$O<\begin{matrix}CH_2\cdot CH(OH)\\ CH(OH)\cdot CH_2\end{matrix}>O \longrightarrow O<\begin{matrix}CH_2\cdot CHO\\ CH(OH)\cdot CH_2OH\end{matrix} \longrightarrow 2CH_2(OH)\cdot CHO$$

In any case, comparison with the kinetic data of McCleland (*loc. cit.*), which were obtained by a cryoscopic method, shows that the second change is the one associated with the actual production of single molecules. It is noteworthy that this reaction involves an expansion with dihydroxyacetone and a contraction with glycollaldehyde. This is probably due to the hydration of the aldehyde group, and it may be compared with the fact that in aqueous solution the conversion of diacetone alcohol into acetone is accompanied by an expansion (Koelichen, *Z. physikal. Chem.*, 1900, **33**, 129), whereas the analogous conversion of aldol to acetaldehyde is accompanied by a contraction (Bell, J., 1937, 1637).

It was found that the first volume change could be eliminated by preliminary treatment with 10^{-4}N-hydrochloric acid, in which the depolymerisation takes place very slowly. About 0·02 g. of glycollaldehyde was weighed out, and 0·324 c.c. of acid added from the type of micropipette described by Bell and Burnett (*Trans. Faraday Soc.*, 1939, **35**, 474). After 15 minutes in the thermostat at 25°, 0·716 c.c. of catalysing solution was added by a second pipette, and the dilatometer filled by suction. The height of the meniscus at *B* was adjusted roughly by applying a piece of filter-paper at *A*; the dilatometer was then closed by forcing a small quantity of

vaselin into the capillary at *A*—this type of seal was entirely satisfactory, and will withstand a considerable pressure difference if necessary. Reliable readings could be obtained a few minutes after addition of the catalyst solution.

With this procedure, the course of the reaction was consistently unimolecular, and the velocity constants were calculated by Guggenheim's method (*Phil. Mag.*, 1926, **2**, 540). Table I gives the details of a typical experiment, the calculated readings being given by $\log_{10}\Delta x = 0{\cdot}274 - 0{\cdot}0123t$. It should be noted that a deviation of 0·01 mm. corresponds to a temperature variation of only 0·005°.

TABLE I.

0·0104N-Glycollic acid + 0·0114N-sodium glycollate + 0·0886N-sodium chloride; Δt = 30 minutes.

Time, mins.	Δx, mm. Obs.	Calc.	Diff., mm.	Time, mins.	Δx, mm. Obs.	Calc.	Diff., mm.	Time, mins.	Δx, mm. Obs.	Calc.	Diff., mm.
11	1·38	1·38	0	20	1·06	1·07	+0·01	29	0·83	0·83	0
12	1·34	1·34	0	21	1·04	1·04	0	30	0·81	0·80	−0·01
13	1·30	1·29	−0·01	22	1·00	1·01	+0·01	31	0·78	0·78	0
14	1·26	1·27	+0·01	23	0·98	0·98	0	32	0·75	0·76	+0·01
15	1·24	1·23	−0·01	24	0·96	0·95	−0·01	33	0·73	0·74	+0·01
16	1·19	1·20	+0·01	25	0·93	0·93	0	34	0·72	0·72	0
17	1·15	1·16	+0·01	26	0·90	0·90	0	35	0·69	0·70	+0·01
18	1·12	1·13	+0·01	27	0·89	0·88	−0·01	36	0·68	0·68	0
19	1·07	1·10	+0·03	28	0·87	0·85	−0·02				

Results.—In Table II, k is a first-order velocity constant in decadic logarithms and minutes, and the concentrations are in moles per litre of solution.

The concentrations of hydrogen and hydroxyl ions in the buffer solutions are calculated as described in the previous paper (Bell and Baughan, *loc. cit.*). The calculated values of k in a buffer solution containing an uncharged acid A and its anion B are based on the equation

$$k = k' + k_A[A] + k_B[B]$$
$$k' = k_0 + k_{H_3O^+}[H_3O^+] + k_{OH^-}[OH^-]$$

For each buffer ratio k' was obtained by graphical extrapolation to zero buffer concentration, and the calculated values of k are obtained from these values of k' and the values of k_A and k_B given in Table III. The values of k' agree to within about 10% with the equation

$$k' = 0{\cdot}0073 + 4{\cdot}76[H_3O^+] + 3{\cdot}15 \times 10^6[OH^-]$$

TABLE II.

Trimethylacetic acid.

$[CMe_3{\cdot}COO^-]$.	10^4k (obs.).	10^4k (calc.).
[A]/[B] = 1·705, $[H_3O^+] = 2{\cdot}4 \times 10^{-5}$, $[OH^-] = 6{\cdot}7 \times 10^{-10}$, $10^4k' = 96$.		
0·0239	137	138
0·0355	158	158
0·0479	180	180
[A]/[B] = 0·533, $[H_3O^+] = 7{\cdot}6 \times 10^{-6}$, $[OH^-] = 2{\cdot}1 \times 10^{-9}$, $10^4k' = 144$.		
0·0198	179	175
0·0198	187	175
0·0406	193	209
0·0552	230	232
0·0798	275	271

Glycollic acid.

$[CH_2(OH){\cdot}COO^-]$.	10^4k (obs.).	10^4k (calc.).
[A]/[B] = 6·63, $[H_3O^+] = 1{\cdot}55 \times 10^{-3}$, $10^4k' = 180$.		
0·0275	263	263
0·0580	350	358
0·0770	426	420
[A]/[B] = 1·213, $[H_3O^+] = 2{\cdot}9 \times 10^{-4}$, $10^4k' = 116$.		
0·0114	123	123
0·0239	132	131
0·0462	144	145
0·0601	154	153
0·0601	148	153

Acetic acid.

$[CH_3{\cdot}COO^-]$.	10^4k (obs.).	10^4k (calc.).
[A]/[B] = 4·706, $[H_3O^+] = 1{\cdot}3 \times 10^{-4}$, $[OH^-] = 1{\cdot}2 \times 10^{-11}$, $10^4k' = 88$.		
0·0209	134	140
0·0367	182	178
0·0477	195	206
0·0633	239	244
0·0719	274	266
[A]/[B] = 0·961, $[H_3O^+] = 3{\cdot}8 \times 10^{-5}$, $[OH^-] = 4{\cdot}2 \times 10^{-10}$, $10^4k' = 88$.		
0·0159	117	118
0·0318	149	148
0·0510	183	185
0·0703	222	222

Monochloroacetic acid.

$[CH_2Cl{\cdot}COO^-]$.	10^4k (obs.).	10^4k (calc.).
[A]/[B] = 0·860, $[H_3O^+] = 1{\cdot}85 \times 10^{-3}$, $10^4k' = 203$.		
0·0156	222	218
0·0517	250	253
0·0707	281	279

Hydrochloric acid.

[HCl].	10^4k (obs.).	10^4k (calc.).
0·0028	192	203
0·0056	343	334
0·0111	613	591
0·0169	914	862

Discussion.

The behaviour of glycollaldehyde is clearly qualitatively very similar to that of dihydroxyacetone. A quantitative comparison is given in Table III, which contains the dissociation constants of the catalysts studied, together with their catalytic constants for the two depolymerisations. The columns headed I refer to that giving glycollaldehyde, and those headed II to that giving dihydroxyacetone.

Table III.

Acid catalysis.				*Basic catalysis.*			
		k_A.				k_B.	
Catalyst.	K_A.	I.	II.	Catalyst.	K_A.	I.	II.
H_3O^+	55·5	4·76	1·72	OH^-	$1·8 \times 10^{-16}$	$3·2 \times 10^{6}$	$4·0 \times 10^{7}$
$CH_2Cl·CO_2H$ ...	$1·4 \times 10^{-3}$	$1·1 \times 10^{-1}$	$1·6 \times 10^{-2}$	$CMe_3·COO^-$ ...	$9·1 \times 10^{-6}$	$1·5 \times 10^{-1}$	$4·2 \times 10^{-1}$
$H·CO_2H$	$1·8 \times 10^{-4}$	—	$5·4 \times 10^{-3}$	$CH_3·COO^-$ ...	$1·8 \times 10^{-5}$	$1·8 \times 10^{-1}$	$1·6 \times 10^{-1}$
$CH_2(OH)·CO_2H$	$1·5 \times 10^{-4}$	$4·6 \times 10^{-2}$	—	$CH_2(OH)·COO^-$	$1·5 \times 10^{-4}$	5×10^{-3}	—
$CH_3·CO_2H$	$1·8 \times 10^{-5}$	$1·5 \times 10^{-2}$	—	$H·COO^-$	$1·8 \times 10^{-4}$	—	$3·2 \times 10^{-2}$
$CMe_3·CO_2H$ ...	$9·1 \times 10^{-6}$	$1·3 \times 10^{-2}$	—	(H_2O	55·5	$1·3 \times 10^{-4}$	$4·6 \times 10^{-5}$)

It will be seen that glycollaldehyde is considerably more sensitive to acids and less sensitive to bases than is dihydroxyacetone. The value of k' passes through a minimum at about $[H_3O^+] = 10^{-4}$, and at this point the velocity is only about 15% greater than the "spontaneous" rate k_0 due to catalysis by water molecules. The data are not sufficiently extensive or accurate (especially for basic catalysis) to give much information about the relation between acid–base strength and catalytic power, but they are consistent with relations of the type due to Brönsted for both acid and basic catalysis, the same exponents as those found for dihydroxyacetone (0·4 and 0·8 respectively) being used.

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