CCVII.—*Bimolecular Glycollaldehyde.*

By NIAL PATRICK McCLELAND.

It has often been the custom to make a distinction between "association" and "polymerisation." The former has been regarded as a physical phenomenon consisting in the aggregation of whole molecules, whereas the latter is generally classed as a chemical process, and the constitution of the polymerised forms is expressed in terms of atomic linking.

At present the prevailing view appears to be that the two phenomena are of the same kind, differing only in degree, and it has been found necessary to evolve hypotheses of "latent," "auxiliary," and "contra" valencies to explain the constitutions of the resulting substances. Practically the question may be merely one of stability, that is to say, the difference between "association" and "polymerisation" as ordinarily defined may lie only in the fact that polymerised forms can be definitely isolated as such between wide limits of temperature, pressure, and so on, whereas the degree of association depends entirely on the conditions.

Now Fenton and Jackson observed (*Trans.*, 1899, **75**, 575) that the molecular weight of crystalline glycollaldehyde in a freshly prepared aqueous solution is 120, that is to say, double the value expected from the formula $\text{HO}\cdot\text{CH}_2\cdot\text{CHO}$, and, further, that it gradually falls to the normal value on keeping.

Similar behaviour has been observed in the related substances glyceraldehyde and dihydroxyacetone by Wohl (*Ber.*, 1898, **31**, 2394) and Bertrand (*Compt. rend.*, 1899, **129**, 341) respectively.

At Dr. Fenton's suggestion the author has investigated this change of state in the case of glycollaldehyde with the object of ascertaining its general character as an association or polymerisation phenomenon in the sense indicated above.

Bertrand concluded that the change observed by him was due to molecular dissociation. He seems to have based his conclusion partly on an observation that the molecular weight of the liquid formed by the melting of crystalline dihydroxyacetone was almost normal in solution, suggesting that the liquid was the unassociated form, and partly on the fact that, although the crystalline substance is sparingly soluble in alcohol and ether, yet on warming it readily dissolves, and does not recrystallise on cooling; reasons are given below for concluding that the former observation is erroneous; the latter can obviously be easily explained otherwise.

Wohl suggested that the crystalline form is a sort of acetal formed from two molecules, thus:

in which case the change in aqueous solution would be due to hydrolysis, with the formation of an ortho-aldehyde.

The investigation was carried out in the following way:

First, the dissociation of glycollaldehyde in aqueous solution was investigated with a view to ascertaining the influence of dilution on the rate.

Next, the molecular state in other solvents was studied. The solvents tried were methyl and ethyl alcohols, acetone, acetonitrile, pyridine, formic and acetic acids.

It was expected that if the change was due to hydrolysis, alcohols would bring it about almost as readily as water, possibly with the formation of acetals of the normal type, the other solvents not at all; whilst on the supposition that the bimolecular state is an example of association, solvents would probably be effective in the order of their dissociating powers.

The vapour density was also determined somewhat above the boiling point, and Mr. Purvis kindly photographed the absorption spectra of the two forms in solution.

The glycollaldehyde was prepared by the method described by Fenton (*Trans.*, 1905, **87**, 817). A pyridine solution is formed from dihydroxymaleic acid, and is distilled in a vacuum; finally, glycollaldehyde crystallises out on nucleating the syrup obtained by evaporating the pyridine in a desiccator. During the latter part of the distillation (when all the pyridine has passed over), crystals are frequently formed in the tube, showing that they can form spontaneously.

Crystals have also been obtained from an aqueous solution, but any trace of impurity seems to prevent their formation.

The glycollaldehyde so obtained melts at 96—97°, forming a syrupy liquid, which, when cooled, does not crystallise for several days. This liquid appears to be identical with the syrup mentioned above. The yield is very poor, about 0.5 to 1 per cent. of the calculated (starting from tartaric acid). Owing to the cost, it was essential to work on a very small scale throughout.

Dissociation Rate in Water.

This was studied by making successive determinations of the apparent molecular weight in aqueous solution, using the cryoscopic method. Between readings, the solution was kept surrounded by ice.

The continual change of temperature necessary for each reading caused the experimental error to be somewhat great.

t = time of observation in minutes after the first reading.

m = calculated molecular weight.

C = concentration of double molecules, taking the initial value as the unit,

so that $C = \frac{M - 60}{60}$,

$k = \frac{1}{t' - t} \log_e \frac{C}{C'}$, where C' and t' refer to the last reading given.

In this way it was hoped that the error due to the fact that it took an appreciable time to dissolve the whole of the substance would be minimised.

The molecular depression for water was taken to be 18.7.

(1) 0.4212 gram of substance in 20.80 of water (1 in 49.4).

t .	Δ .	m .	C .	k .
—	0.387	114.1	0.902	0.0023
30	0.401	110.1	0.835	0.0020
60	0.417	106.1	0.768	0.0020
95	0.429	103.0	0.717	0.0020
130	0.438	101.0	0.683	0.0021
160	0.449	98.5	0.642	0.0021
220	0.471	93.9	0.565	0.0022
270	0.489	90.4	0.507	—

Mean, $k = 0.00210$.

(2) 0.1831 gram in 16.56 (1 in 90.4).

t .	Δ .	m .	C .	k .
—	0.182	113.6	0.873	0.0030
60	0.198	104.4	0.740	0.0030
130	0.219	94.4	0.573	0.0028
190	0.231	87.4	0.457	0.0023
315	0.256	80.8	0.347	0.0033
330	0.259	79.8	0.330	—

Mean (excluding 4th value), $k = 0.00303$.

(3) 0.1128 gram in 31.91 (1 in 283).

It was found that $k=0.00561$.

The above results show that the reaction is, as might be expected, unimolecular, that is, $C_4H_8O_4 \rightarrow 2C_2H_4O_2$, and that the rate increases with the dilution.

The effect of temperature has not been studied quantitatively, but it has been observed that at 20° the change takes place with extreme rapidity.

So far as can be observed, the dissociation in dilute solutions is complete, but since crystals can be obtained from an aqueous solution it follows that association must take place in strong solutions.

The Liquid Form in Water.

The molecular weight in water was determined.

	Solvent (grams).	Substance (gram).	Δ^t .	M. W.	
1.	25.02	0.1946	0.118	123.0	fresh solution
			0.139	100.8	} on keeping
			0.149	97.4	
2.	15.43	0.1049	0.119	106.9	fresh solution
			0.194	65.5	on keeping

Whence it appears that the liquid form exhibits the same behaviour as the solid form.

Bertrand states, as mentioned above, that the molecular weight of a solution in water of liquid dihydroxyacetone is almost normal (105, normal value=90). He mentions, however, that it took twenty-five minutes to cool the solution to freezing point. If, as appears possible, he started with the solution at the ordinary temperature, it is natural that dissociation would take place very rapidly at first.

Molecular State in Solvents other than Water.

The solvents are taken in the order of their dissociating powers. All were purified carefully before using.

Formic Acid.

The cryoscopic method was used for this solvent. Const.=27.7.

Solvent (grams).	Substance (gram).	Δ^t .	M. W.
22.13	0.1517	{ 0.279	67.5
		{ 0.439	42.9

That the molecular weight falls below 60 may be explained by assuming that esterification takes place in addition to dissociation,

one molecule of bimolecular glycollaldehyde giving rise to 4 molecules, 2 of unimolecular formate and 2 of water.

The same results were obtained when acetic acid was used as solvent; it was noticed that the apparent molecular weight gradually sank to 30.

It is concluded that in formic and acetic acids dissociation readily takes place, apparently accompanied by esterification.

Methyl Alcohol.

The molecular weight was observed by the boiling-point method, using Beckmann's apparatus.

The molecular elevation is 8.80.

	Solvent (grams).	Substance (gram).	E.	M.W.	
1.	40.61	0.2163	0.058 0.074	81.0 63.5	after 30 minutes' boiling 50 " "
2.	40.02	0.2828	0.059 0.079 0.091	105.6 79.0 68.5	" 15 " " " 30 " " " 45 " "

It appears, then, that dissociation takes place in methyl alcohol on boiling, although far less rapidly than in water and formic acid.

The experimental error was too great to permit the rate to be determined satisfactorily.

Acetonitrile.

The pure solvent boiled at 80.0°. The molecular elevation is 14.39.

	Solvent (grams).	Substance (gram).	E.	M.W.	
1.	40.92	0.2898	0.090 0.134	113.0 76.0	after 20 minutes' boiling 45 " "
2.	20.38	0.3330	0.156 0.178 0.201 0.236	108.2 95.0 84.0 71.6	" 20 " " " 40 " " " 60 " " " 90 " "

Therefore, dissociation takes place in acetonitrile somewhat less rapidly than in methyl alcohol.

Ethyl Alcohol.

The molecular weight in a fresh solution was found by using Walker's method:

0.3871 gram in 15.8 c.c. gave E 0.31°. M.W. = 123.1.

0.1560 " 19.5 c.c. " E 0.11°. M.W. = 113.5.

A solution was then boiled under reflux for five hours. After this time the molecular weight was determined, and it was found that almost complete dissociation had taken place:

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0.4004 gram in 32.39 grams gave E 0.180°. M.W.=79.0.

0.4004 „ 32.39 „ „ E 0.192°. M.W.=74.1 thirty-five minutes later.

Acetone.

A solution was boiled for five hours, as before.

Substance (grams).	Solvent (gram).	E.	M.W.
32.39	0.4004	0.192	106.0
		0.197	103.6
37.96	0.2660	0.136	85.0

A solution kept at the ordinary temperature for three weeks showed no trace of dissociation.

Pyridine.

The molecular state in pyridine was determined by Blackman's method (Trans., 1904, 85, 1474) under diminished pressure, using carbamide (M.W.=60) as comparative substance. The results appeared to indicate that the substance was dissociated.

Vapour Density.

Hofmann's method was employed.

Since glycollaldehyde on heating tends to polymerise into a brown gum, it was necessary to heat rapidly; even so, however, traces of "browning" appeared.

This rapid heating prevented the mercury from being properly heated throughout. These two errors tend to cancel one another, and no allowance has been made for them.

The heating liquid used was aniline, which boils at 182°.

This temperature is well above the boiling point of glycollaldehyde, which observations in a vacuum place in the neighbourhood of 150°:

(1) 0.0218 gram gave 48.6 c.c. of vapour at 182°.

Barometer's height, 782 mm.

Height of mercury column, 602 mm. Correction for expansion, 19 mm.

Vapour pressure of mercury at 182°=12 mm.

So pressure of the vapour=187 mm.

Hence vapour density=33.8.

(2) 0.0141 gram gave 43.7 c.c. of vapour at 182°.

Barometer height, 758 mm.

Height of mercury column, 622 mm. Correction, 20 mm.

So pressure of the vapour=144 mm.

Hence vapour density=31.5.

The vapour is therefore unassociated about 30 degrees above the boiling point.

The above results, namely, dissociation in solvents usually classed as dissociating, some of which have no hydrolysing power, coupled with dissociation in the vapour state, and with return to the bimolecular state on condensation, appear to point to the conclusion that in the bimolecular state we are dealing with the phenomenon of association, that is, linking of two whole molecules, rather than chemical interaction between them. The abnormal feature of this case lies in the fact that dissociation is by no means immediate. It is possible, however, that in other cases, where a substance has been found partly associated in a solvent, true equilibrium may not have been reached.

An observation has been made, showing a chemical difference between the two forms.

Action of Phenylhydrazine.

When phenylhydrazine is added to an aqueous solution, a yellow osazone (m. p. 169—170°) separates; if, however, phenylhydrazine is added to a fresh alcoholic solution, no action whatever takes place, and on evaporating the alcohol the aldehyde appears to have dissolved in the phenylhydrazine.

This suggests that the CO group is absent from the associated form.

Absorption Spectrum.

A *N*/100-solution in alcohol of the solid glycollaldehyde was made, and its absorption spectrum observed in the usual way, through varying thicknesses.

Four well-marked bands were observed, and through a thickness of 15 mm. the centres of maximum absorption of the bands were λ 2615, λ 2550, λ 2495, λ 2445, and through a thickness of 42 mm. general absorption began at λ 2645.

A *N*/100-solution in water was also examined; no bands were observed. The positions at which general absorption began through 15 mm. and 45 mm. were λ 2270 and λ 2290 respectively.

These results prove that the conditions of the dissolved substances were entirely different in the two cases (for it is extremely unlikely that the bands are due to the solvent itself).

Specific Gravity and Refractive Power of the Liquid Form.

At 100, 0.2035 c.c. weighed 0.2729 gram. $D=1.372$.

0.3158 c.c. „ 0.4300 „ $D=1.361$.

Mean.....1.366.

At 16° the density was obtained by measuring the length which a known weight of the liquid form occupied in a calibrated tube.

It was found that 0.6122 gram of mercury occupied 5.72 cm. of the tube,

and (1) 0.1540 gram substance occupied 14.12 cm. $D = 1.385$.

(2) 0.1277 " " " 11.60 cm. $D = 1.397$.

Mean.....1.391.

From the above, by extrapolation, the density at 11° = 1.393.

At 11° it was observed that $\mu_w = 1.4811$ (Lorentz formula).

Hence $M_D = 24.51$.

Twice the calculated value for $\text{HO}\cdot\text{CH}_2\cdot\text{CHO}$ is 26.39.

From the above results the author concludes that the abnormal molecular weight of glycollaldehyde in the pure form is due to a phenomenon which is on the border line between "association" and "polymerisation," that is, association where the associated form is not extremely unstable.

It is suggested that the constitution in the bimolecular state is represented by the formula $\text{HO}\cdot\text{CH}_2\cdot\text{CH} \begin{smallmatrix} \text{O} \\ \diagup \diagdown \\ \text{O} \end{smallmatrix} \text{CH}\cdot\text{CH}_2\cdot\text{OH}$, the calculated value for the refractive power for which is 24.82 (not making any allowance for the ring formation), agreeing fairly well with the observed value. Similar formulæ suggest themselves in the cases of crystalline dihydroxyacetone and glyceraldehyde. Support is given to this hypothesis by the fact that some ketones (where no acetal formation is possible) and amides are associated. Aldehydes also appear to be capable of bimolecular association, for it has been observed that when gaseous formaldehyde is passed into chloroform (an extremely non-dissociating solvent) a substance having the formula $\text{C}_2\text{H}_4\text{O}_2$ is obtained (*Pharm. Zeit.*, 1904, **49**, 608). In these cases the cohesion between the two molecules is far less intense than in the case considered above, in which it perhaps is due to some influence exerted by the hydroxyl group.

If the above constitution is assumed, the behaviour of the substance can be completely accounted for.

In the first place, it appears that solutions which give rise to absorption bands in the ultra-violet are generally those of substances which contain unsaturated rings admitting of alternations of linking, the bands being perhaps due to vibrations from one form of linking to another. In the case of glycollaldehyde, this can occur through

the alternation of the forms $\text{C} \begin{smallmatrix} \text{O} \\ \diagup \diagdown \\ \text{O} \end{smallmatrix} \text{C}$ and $\text{C}:\text{O}:\text{O}:\text{C}$. Secondly, it

appears probable that a system of the above type is not very firmly linked up, and therefore will be liable to rupture if intense vibrations are set up.

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It is suggested that solvents have the power either to intensify or damp the vibrations of the molecules of solutes, on account of the vibrations of their own molecules. Where the vibrations are intensified the solvent is a dissociating one, and it is particularly noticeable that those solvents are most strongly dissociating the molecules of which are most strongly associated, and so are in a state of vibration of a character similar to those of the solute.

In conclusion, the author desires to record his great indebtedness to Dr. Fentón for his very kind advice throughout the work, and to Mr. Purvis for photographing the absorption spectra and suggesting their interpretation.

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