110. *The Polymerisation of Methylglyoxal.*

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A study of the preparation and physical properties (refractive index, density, surface tension, and heat of combustion) of pure, dry, freshly distilled methylglyoxal and of both dry and wet polymerised samples has shown that the speed of polymerisation is greatly affected by traces of moisture. The results do not indicate the preferential formation of any particular polymer, but rather the progressive building up of structures of high molecular weight. Although methylglyoxal undoubtedly combines with water, the rate of polymerisation in the presence of water makes the isolation of a definite hydrate impossible.

METHYLGLYOXAL, when freshly prepared and dry, is a mobile volatile liquid. It polymerises, on standing, to a hard glass, more or less rapidly according to its purity. The factors affecting this polymerisation, though the subject of speculation, have not hitherto been clearly understood. The polymerisation of glyoxal, the first member of the series of 1 : 2-diketones, has long been known to be affected greatly both in speed and in end-point by the presence of traces of moisture. If glyoxal is thoroughly dried by distillation from phosphoric oxide, the speed of polymerisation is slow, whereas the addition of a trace of moisture, or dissolution in solvents containing water, causes the instantaneous formation of paraglyoxal $(C_2H_2O_2)_n$ (Harries and Temme, *Ber.*, 1907, **40**, 167). Evaporation of a dilute aqueous solution of monomeric glyoxal brings about the formation of another polymer, polyglyoxal (Debus, *Annalen*, 1857, **102**, 205). Diacetyl, on the other hand, does not polymerise at an appreciable rate on standing, nor does water cause any change. Ice-cold potassium hydroxide solution slowly transforms it into a dimer (Diels, Blanchard, and Heyden, *Ber.*, 1914, **47**, 2357), whereas several days' shaking with cold concentrated hydrochloric acid gives a trimer.

During the preparation of methylglyoxal by oxidising acetone with selenium dioxide (Riley, Morley, and Friend, J., 1932, 1875), it was noticed that its speed of polymerisation, as indicated by its rate of setting to a hard glass, varied considerably and was apparently largely determined by the purity of the product. The above-mentioned properties of glyoxal and diacetyl suggest that methylglyoxal would behave in an intermediate manner and that its rate of polymerisation would be affected by traces of moisture, though probably not to the same extent as with glyoxal.

The preparation and properties of pure, anhydrous methylglyoxal have received little attention, most of the earlier workers being content to prepare either dilute aqueous solutions or only partly dehydrated compounds (compare, *inter alia*, v. Pechmann, *Ber.*, 1887, **20**, 3316; Harries and Turk, *ibid.*, 1905, **38**, 1632; Harries and Temme, *ibid.*, 1907, **40**, 172). Anhydrous, monomeric methylglyoxal was obtained by Meisenheimer (*ibid.*, 1912, **45**, 2635) and by Fischer and Taube (*ibid.*, 1926, **59**, 851) by distilling the polymer in a vacuum and passing the vapour over calcium chloride. This method of purification was employed in the present work, the crude methylglyoxal being obtained from acetone by the method of Riley, Morley, and Friend (*loc. cit.*). The product was an intensely yellow, mobile, volatile liquid, which polymerised only slowly if kept in a sealed tube, becoming of glycerol-like consistency in a fortnight and setting to a hard glass in about 10 weeks.

Molecular Weight and Hydrates.—The determination of the vapour density of methylglyoxal by Fischer and Taube (*loc. cit.*) indicated that the vapour was monomeric. The results of cryoscopic determinations in various solvents show discrepancies which are probably accounted for by differences in the extent of the polymerisation of the compounds used. The results of various workers are summarised in Table I, and this evidence suggests that pure freshly distilled methylglyoxal dissolves in water and in benzene in the monomeric condition, and that the dry polymerised variety slowly depolymerises in aqueous solution. The existence of the hydrates suggested by Hahn and Schales and by Bersin is open to doubt because of the indefinite nature of the wet polymerised

TABLE I.

Description of material.	Solvent.	*M.*	Inferences.
Wet, polymerised	HOAc	302	Tetramer [1]
Dry, freshly distilled	C_6H_6	125	Dimer [2]
,, ,,	H_2O	72	Monomer [2]
,, ,,	$CHBr_3$	159, 122	Dimer [2]
Dry, polymerised	H_2O	216 *	Trimer [3]
		88, 72 †	Monomer [3]
Wet, polymerised	HOAc	680—730	$8C_3H_4O_2,4H_2O$ [4]
,, ,,	H_2O	131	Dimer $(2C_3H_4O_2,2H_2O)$[5]
,, ,,	HOAc	31	Dissociated hydrate [5]
Dry, freshly distilled	H_2O	79	Monomer [6]
,, ,,	C_6H_6	70	Monomer [6]

* Immediately on dissolution. † One day later.

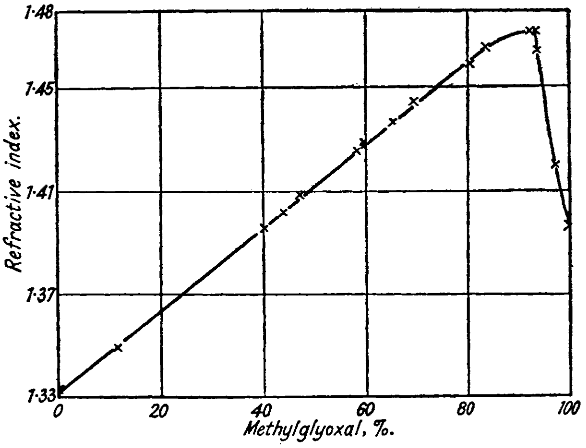
[1] Harries and Turk (*loc. cit.*). [2] Fischer and Taube (*Ber.*, 1924, **57**, 1506; 1926, **59**, 851). [3] Meisenheimer (*loc. cit.*). [4] Hahn and Schales (*Ber.*, 1934, **67**, 1816). [5] Bersin (*ibid.*, 1936, **69**, 560). [6] This paper.

compounds employed. Dilute aqueous solutions of methylglyoxal are colourless when cold, but become green on warming, indicating the existence of an unstable hydrate in the cold aqueous solution, which dissociates at higher temperatures. Neuberg and Schou (*Biochem. Z.*, 1927, **191**, 469), from a study of the ultra-violet absorption spectrum, suggest the existence of a hydrate, probably $CMe(OH)_2{\cdot}CHO$, in aqueous solution.

Refractive Indices of Methylglyoxal and its Aqueous Solutions.—Pure, dry, freshly distilled methylglyoxal had $n_{\mathrm{D}}^{25^\circ}$ 1·3327, compared with 1·3951 increasing to a constant maximum 1·4733 obtained by Fischer and Taube (*loc. cit.*) at 25°, and 1·4572 increasing to 1·4679 for the wet material found by Hahn and Schales (*loc. cit.*) at 20°. The refractive indices found for aqueous solutions of methylglyoxal are given in Table II. These values are plotted against the percentage composition in the figure. The sharp maximum at 1·4721, which is in approximate agreement with the maximum reported by Fischer and Taube (1·4733), occurs at the composition 93·5% methylglyoxal and 6·5% H_2O, corresponding to $C_3H_4O_2,0{\cdot}278H_2O$. This does not suggest the existence of a definite hydrate. It is also significant that when moist methylglyoxal is fractionally distilled in a vacuum, the purest fractions which can be obtained without passing the vapour over a dehydrating agent during distillation contain approximately $0{\cdot}25H_2O$.

TABLE II.

Methylglyoxal, % by wt.	0·0	11·57	40·24	43·91	47·14	58·42	59·66	59·70	65·62
Mol.-fraction	0·0	0·3163	0·1437	0·1637	0·1818	0·2599	0·2696	0·2703	0·3221
$n_{\mathrm{D}}^{25^\circ}$	1·3327	1·3491	1·3957	1·4019	1·4085	1·4259	1·4273	1·4290	1·4367
Methylglyoxal, % by wt.	69·72	80·53	83·72	$92{\cdot}51_5$	93·72	93·77	97·19	100·00	
Mol.-fraction	0·3650	0·5081	0·5593	0·7553	0·7662	0·7837	0·8621	1·000	
$n_{\mathrm{D}}^{25^\circ}$	1·4438	1·4592	1·4658	1·4718	1·4721	1·4645	1·4200	1·3964	



The value $n_{\mathrm{D}}^{25^\circ}$ 1·3327 gives $[R_L]_{\mathrm{D}}$ 16·68 for the molecular refraction of monomeric methylglyoxal, whereas, on the basis of Eisenlöhr's atomic refractivities (*Z. physikal. Chem.*, 1911, **75**, 585), its enolic form should have $[R_L]_{\mathrm{D}}$ 17·123 and its keto-form $[R_L]_{\mathrm{D}}$ 16·076. The corresponding values for dimeric methylglyoxal are: Found, 33·36. Calc. for $CH_3{\cdot}CO{\cdot}CH(OH){\cdot}CH_2{\cdot}CO{\cdot}CHO$, 31·47; and for $CH_2{:}C(OH){\cdot}CH(OH){\cdot}CH{:}C(OH){\cdot}CHO$, 33·56. These values suggest the presence of both forms in the liquid.

Density, Surface Tension, and Parachor.—The determination of the density of methylglyoxal is complicated by its hygroscopic nature and tendency to polymerise. Precautions were taken to avoid the introduction of errors from these sources, and a value of 1·0383 was obtained; Fischer and Taube (*loc. cit.*) found 1·0455. As methylglyoxal contracts on polymerisation, and as this is accelerated by the presence of traces of moisture, it may be assumed *a priori* that the lower value is more nearly correct.

With similar precautions to exclude moisture and prevent polymerisation, surface-tension determinations gave a value of 28·05 dynes/cm. These values give the parachor of monomeric methylglyoxal as [*P*] = 160·2 (Calc.: [*P*] = 169·2, on Sugden's values for the atomic parachors; see "The Parachor and Valency," Routledge, London, 1930). For a dimeric methylgloxal [*P*] = 320·3 (Calc.: 315·2). These results suggest that the dry, freshly distilled liquid is a mixture of the monomer and the dimer.

Heat of Combustion.—The method employed gave heats of combustion with a maximum error of ± 0·3%. Dry, freshly distilled methylglyoxal at 20° exploded spontaneously when the oxygen pressure in the bomb used reached about 22 atm. This explosion occurred several times, once at an oxygen pressure of 19 atm., once at 25 atm., and ten times between 20 and 23 atm. In some cases the silica crucible employed was shattered. Spontaneous combustion did not occur with the wet or the dry polymerised sample. The explosions were probably due to peroxide formation. It is well known that aldehydes, ketones, alcohols, and ethers undergo auto-oxidation (cf. Milas, *Chem. Reviews*, 1932, **10**, 295), and Jorissen and van der Beek (*Rec. Trav. chim.*, 1926, **45**, 245) have isolated a peroxide formed during the auto-oxidation of benzaldehyde. Semenoff (*Chem. Reviews*, 1928, **6**, 347) has shown that peroxide formation in certain chain reactions under increased oxygen pressure may lead to explosions.

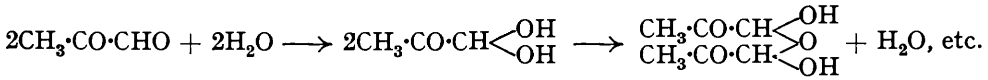
With methylglyoxal, peroxide formation may occur at both the ketonic and the aldehydic group, leading to the formation of an extremely unstable compound. That spontaneous combustion does not occur with the wet or polymerised samples is readily understood, for hydrate formation or polymerisation will occur at the active centres where peroxide formation occurs with the dry unpolymerised material. The results obtained are shown below.

Description of sample.	Heat of combustion, kg.-cals./g.-mol.
Dry, freshly distilled	344·9
Dry, 11 weeks old, vitreous	337·3
$C_3H_4O_2,\frac{1}{3}H_2O$, polymerised, vitreous	331·1
$C_3H_4O_2,\frac{2}{3}H_2O$, polymerised, very viscous	330·0
$C_3H_4O_2,H_2O$, polymerised, very viscous	328·9

The following values for the heat of combustion of methylglyoxal (in kg.-cals./g.-mol.) have been obtained by previous workers: 330 (v. Euler and Linder, "Chemie der Hefe und der alkoholischen Gärung," p. 248, Leipzig, 1915, indirect estimation); 333·7 (Aubel, *Compt. rend.*, 1926, **183**, 573, by calculation, the heat of formation being assumed to be 86); 326 (Fromageot and Emami, *Bull. Soc. chim.*, 1931, **49**, 929, by an indirect method); 345·7 (Neuberg and Hoffman, *Biochem. Z.*, 1932, **252**, 440). The last value was obtained from dry, freshly distilled methylglyoxal prepared by the method of Fischer and Taube (*loc. cit.*), and agrees well with the value obtained in the present investigation.

The values for the heat of combustion given above indicate that the pure, dry, freshly distilled methylglyoxal undergoes a slow polymerisation involving the evolution of approximately 8 kg.-cals. in the course of 11 weeks. The substance containing $\frac{1}{3}H_2O$, which sets rapidly to a vitreous solid, has a heat of combustion 6·2 kg.-cals. less than the dry vitreous variety. This further decrease in the heat content is due either to more extensive polymerisation or to hydrate formation, or possibly to both these factors. It is perhaps adventitious that the further decrease in the heat content shown by the sample containing an additional $\frac{2}{3}H_2O$ is exactly twice the decrease shown by the sample containing an additional $\frac{1}{3}H_2O$, and it would be unwise, owing to the complicated nature of the system, to conclude from this that the heat of hydration of methylglyoxal is 3·3 kg.-cals. The results suggest, however, that the heat effect of hydration will be of this order.

Although methylglyoxal forms an azeotropic mixture with water of the approximate composition $C_3H_4O_2,0{\cdot}28H_2O$, and although hydrates do undoubtedly exist in the liquid phase at room temperature of sufficient stability to be undecomposed by calcium chloride, yet the rapid polymerisation which occurs in the presence of water makes the isolation of any definite hydrate impossible. The preparation of monomeric, or only slightly polymerised methylglyoxal is possible by careful exclusion of water in the final stages and by the vapour phase dehydration with calcium chloride during distillation. The use of phosphoric oxide is not recommended, as this causes sufficient decomposition to introduce appreciable amounts of water into the product. Even the dry material polymerises slowly, possibly owing to the presence of minute traces of water. This, and the fact that the addition of water brings about a pronounced increase in the rate of polymerisation, suggests that the mechanism of the process is as follows :



$$2CH_3{\cdot}CO{\cdot}CHO + 2H_2O \longrightarrow 2CH_3{\cdot}CO{\cdot}CH{<}^{OH}_{OH} \longrightarrow \begin{matrix} CH_3{\cdot}CO{\cdot}CH{<}^{OH}_{O} \\ CH_3{\cdot}CO{\cdot}CH{<}^{O}_{OH} \end{matrix} + H_2O, \text{ etc.}$$

The rapid polymerisation of glyoxal itself, and the fact that diacetyl does not polymerise, suggest that the aldehyde group and not the ketone group is the active centre in bringing about the polymerisation of methylglyoxal. The formation of a hard glass suggests the presence of cross linkages in the polymerised substance. These are possibly formed through the agency of polymers such as $CH_3{\cdot}CO{\cdot}CH(OH){\cdot}CH_2{\cdot}CO{\cdot}CHO$.

The results do not indicate the preferential formation of any particular polymer, but rather the progressive building up of structures of high molecular weight. The physical constants indicate the presence of both keto- and enolic forms in the unpolymerised liquid.

EXPERIMENTAL.

Crude methylglyoxal was prepared by the method described by Riley, Morley, and Friend. A fraction (50 c.c.) of fairly pure methylglyoxal boiling at 103—110° at atmospheric pressure, which was initially a mobile liquid and in the course of ½ hour after distillation had become very viscous with the evolution of considerable heat, was dissolved in dry ether and dried for 24 hrs. over sodium sulphate. After removal of solvent, the residue was distilled in a vacuum, and a fraction, b. p. 57—60°/20 mm., collected, the receiver being cooled in liquid air. On warming the receiver to room temperature, it was seen in some preparations to contain two layers, the uppermost being more mobile and yellow. This was poured off, and in 2 days it set to a hard glass. Typical analyses of different specimens were : C, 47·3, 47·7, 47·0; H, 6·1, 5·8, 5·9 (Calc. for $C_3H_4O_2,\frac{1}{4}H_2O$: C, 47·0; H, 5·9%). The separation into two layers was probably connected with the effect of traces of water on the rate of polymerisation. The lower layer had a similar composition to the upper. The residual water could not be removed by dehydration of the liquid or its ethereal solution with sodium sulphate, potassium carbonate, calcium chloride, or phosphoric oxide. The use of the last two reagents diminished the yield. The best results were obtained by distilling the above fraction under very low pressure, passing the vapour over calcium chloride granules, freshly dried at 260°, and condensing the distillate by means of liquid air. The distillation was repeated twice, the final product being a yellow, mobile, pungent liquid. It remained so for 3 days after distillation; it then gradually became less mobile, and in 3 weeks it had the consistency of glycerol; in 6 weeks it flowed very slowly, and in 10 weeks it had set to a hard glass comparable with that given by $C_3H_4O_2,\frac{1}{4}H_2O$. During this time the colour changed from deep yellow to greenish-yellow. The glass dissolved in many organic solvents giving green solutions, and in water giving a colourless solution (Found : C, 49·8, 49·4; H, 5·6, 5·55. Calc. for $C_3H_4O_2$: C, 50·0; H, 5·6%).

The molecular-weight determinations were made by Beckmann's cryoscopic method in benzene and water, a freshly distilled sample of the methylglyoxal being used.

The refractive indices were determined by means of an Abbé refractometer, the prisms being at 25° ± 0·25°. The mixtures of water and methylglyoxal were made up in a small weighing bottle. Care was necessary in making up the mixture containing 7% H_2O as this set rapidly to a hard glass with considerable evolution of heat. If the water was added quickly the mixture boiled very vigorously.

The density determinations were carried out by distilling the sample directly into a small specific gravity bottle cooled in liquid air. The bottle was then placed in a test-tube and allowed to attain a temperature of 25° in a thermostat, care being taken to prevent the access of moisture. A check determination was carried out on a sample of pure benzene.

The surface tension of freshly distilled methylglyoxal was determined at 25° by the capillary rise method, precautions being taken to exclude every trace of moisture.

A Mahler–Kroecker bomb, kindly lent by Dr. J. H. Jones, of the Coal Survey Laboratory (D.S.I.R.), King's College, Newcastle-upon-Tyne, was employed in determining the heats of combustion of the various samples of methylglyoxal. Ignition was effected by 1" of cotton thread fastened to a piece of platinum wire connected to the two electrodes and dipping into the sample in the crucible. The heat of combustion of the cotton (11 cals.) was allowed for. Check determinations using medicinal paraffin were carried out. Because of the vigorous manner in which pure, dry methylglyoxal burns, incomplete combustion may occur, due to the scattering of the sample. Fischer and Taube (*loc. cit.*) had noted this. To overcome this difficulty, about 0·5 g. of the sample was weighed from a well-stoppered weighing bottle into the bomb crucible and immediately covered with a similar amount of medicinal paraffin. This was placed in the bomb, which was then screwed up, all these operations being carried out as rapidly as possible. The mixture burned completely in an oxygen pressure of 18 atm. A standardised Beckmann thermometer was used, and the usual cooling corrections were employed.

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