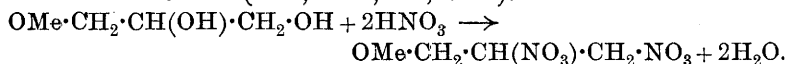# VII.—*Glyceryl Methyl Ether Dinitrate* (*a-Methylin Dinitrate*.)

By David Trevor Jones.

During recent years, considerable attention has been devoted to the study of the mono- and di-nitrates of glycerol and their chlorides and ethers. The interest in these substances has been stimulated by the technical possibilities which they appeared to offer as ingredients of non-freezing nitroglycerin blasting compositions. Among the substances investigated have been the dinitrate of monochlorohydrin (Kast, *Zeitsch. ges. Schiess- u. Sprengstoffw.*, 1906, **1**, 227), which has been more or less extensively used in such explosives as gelatin astralit, gelatin westfalit, etc. The mono- and di-nitrates of glycerol have been very exhaustively studied by Will (*Ber.*, 1908, **41**, 1107), who commenced the investigation of these substances with the above-mentioned technical object in view. The dimethyl and diethyl ethers of glycerol mononitrate have been described by Paternò and Benelli (*Gazzetta*, 1909, **39**, ii, 312), whilst Vender has described the dinitrates of monoacetin and monoformin (*Zeitsch. ges. Schiess- u. Sprengstoffw.*, 1907, **2**, 21).

Glyceryl methyl ether dinitrate, which is here described, was prepared by the direct nitration of the *a*-monomethyl ether of Grün and Bockisch (*Ber.*, 1908, **41**, 3471).

$$OMe \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot OH + 2HNO_3 \longrightarrow$$
$$OMe \cdot CH_2 \cdot CH(NO_3) \cdot CH_2 \cdot NO_3 + 2H_2O.$$

The product, which was readily isolated, was found to solidify after being well supercooled and stirred. It is a powerful explosive, having about two-thirds the strength of nitroglycerin. It is, however, much less sensitive to shock, although rather more readily exploded by heat. Its effect in lowering the freezing point of nitroglycerin is much the same as that of molecular concentra-

tions of monochlorohydrin dinitrate (Kast, *loc. cit.*) and of ethyl nitrate (Nauckhoff, *Zeitsch. angew. Chem.*, 1905, **18**, 21). All these values, however, are in complete disagreement with the value for the freezing-point constant of nitroglycerin as calculated from a carefully conducted determination of its latent heat of fusion (Hibbert and Fuller, *J. Amer. Chem. Soc.*, 1913, **35**, 979).

The substance did not appear to exist in a second or labile form corresponding with the labile form of nitroglycerin.

E x p e r i m e n t a l.

Glyceryl a-monomethyl ether was prepared by Grün and Bockisch's method (*loc. cit.*). The product distilled at 120°/ 18 mm., and the yield was 127 grams, or from 200 grams of mono-chlorohydrin 66 per cent. of the theoretical. The same yield was obtained on repeating the experiment.

Glyceryl Methyl Ether Dinitrate.

Sixty-three grams of glyceryl a-monomethyl ether were gradu-ally added to 480 grams of a mixture of nitric and sulphuric acids ($HNO_3 = 38·6$, $H_2SO_4 = 59·0$, $H_2O = 2·4$ per cent.), which was cooled in ice-water during the nitration. The initial temperature was 13°. During the operation, the temperature was allowed to rise to 20°, and was maintained at that point until the end. The nitration proceeded quite smoothly, and was easily controlled by regulating the addition of the glyceryl methyl ether. The time occupied by the nitration was from twenty to twenty-five minutes. The product was completely soluble in the mixed acid, and the mixture was slowly poured into 800 c.c. of water, the temperature being allowed to rise to 40°. The bulk of the dinitrate separated, and, after remaining for some little time, the bulk of the aqueous layer was poured off and preserved for extraction. The residue containing the dinitrate was neutralised with a semi-saturated solution of sodium carbonate. The dinitrate was then run off from below, the neutralised aqueous layer being added to the diluted acid which had been previously poured off. The dinitrate was then washed three times at 50° with an equal bulk of 5 per cent. sodium carbonate solution, then three times with water, and was finally dried in a desiccator over calcium chloride. The yield was 75 grams, or 64 per cent. of the theoretical. The neutralised aqueous washings were extracted with ether, and the ethereal solution was washed with 5 per cent. sodium carbonate solution, dried with calcium chloride, filtered, evaporated under diminished

pressure, and preserved over calcium chloride in a desiccator. In this way, a further yield of 13·9 grams was obtained, the total yield being thus 88·9 grams, or 77 per cent. of the theoretical.

The dry liquid constituting the first and major portion of the yield was analysed by the combustion method, but on account of its highly explosive nature the weighed-out substance was first converted into a weak dynamite by mixing with excess of previously ignited kieselguhr, the dynamite in turn being mixed with roughly powdered copper oxide and introduced into the combustion tube. The combustion proceeded normally.

The nitrogen was estimated by the nitrometer method, using sulphuric acid, as in the analysis of guncotton :

0·1397 gave 0·1248 CO_2 and 0·0514 H_2O. $C = 24·36$; $H = 4·03$.
0·5492 ,, 132·3 c.c. NO at 16° and 755 mm. $N = 14·15$.
0·638 in 20·45 benzene gave $\Delta^t = -0·833°$. M.W. $= 188$.
$C_4H_8O_7N_2$ requires $C = 24·28$; $H = 4·08$; $N = 14·29$ per cent.
M.W. $= 196$.

The substance was therefore undoubtedly α-methylin dinitrate.

Glyceryl methyl ether dinitrate crystallises in white, monoclinic prisms melting at 24°. As first obtained, it was a clear, colourless liquid, which became pale yellow on keeping. It crystallised with difficulty, and remained liquid, even with occasional shaking, for more than two years in a magazine maintained at 15—21°. It distilled at 124°/18 mm., that is, at approximately the same temperature as the glyceryl methyl ether from which it was derived, and some 22° lower than glyceryl dinitrate, the corresponding alcohol.

It is therefore more volatile than nitroglycerin, and when tested at 100° on a watch-glass it was found to volatilise at from seven to eight times as rapidly. The liquid has D_{15}^{15} 1·374 and n_D^{21} 1·4478. It is soluble in benzene, toluene, acetic acid, methyl and ethyl alcohols, chloroform, ether, or acetone, and insoluble in carbon disulphide or light petroleum.

It gelatinises nitro-cotton rapidly at the ordinary temperature, and after warming it yields a gelatin softer and more plastic than that obtained from nitroglycerin.

The chief interest of this substance lies in its explosive properties as compared with those of nitroglycerin. It has about two-thirds the power of nitroglycerin, although it is much less sensitive to shock. Its comparative insensitiveness was demonstrated by submitting to the fall-hammer test unfrozen dynamites each containing three parts of explosive to one part of kieselguhr. Both substances were placed under a steel disk and subjected to the

impact of a weight of 1 kilogram, falling from a measured height. The results are set forth in the following table:

Dinitrate.			Nitroglycerin.		
Height of fall. cm.	Detonations.	Failures.	Height of fall. cm.	Detonations.	Failures.
100	2	8	30	10	0
95	1	9	20	10	0
90	1	9	15	9	1
85	0	10	10	0	10

The solid substance was very insensitive. It did not explode even when scratched with the sharp edge of a thin melting-point tube. On the other hand, the dinitrate proved to be more easily exploded when heated than did nitroglycerin. When heated in a glass test-tube in a metal-bath, the temperature being raised at the rate of 5° per minute, it was observed to explode at 182°, the trinitrate exploding at 192°.

Comparative power tests of nitroglycerin and methylin dinitrate dynamites were made with the Trauzl lead block and mortar tests. In the lead block, the dinitrate dynamite gave an expansion of 22·9 c.c., a similar charge of nitroglycerin dynamite giving 30·0 c.c. In the mortar test, the relative powers indicated by the ballistic pendulum were 93·76 kilogram-metres (678 foot-lb.) for the dinitrate dynamite as compared with 124·43 kilogram-metres (900 foot-lb.) for a similar charge of nitroglycerin dynamite. Methylin dinitrate, therefore, would appear to have rather more than two-thirds the strength of nitroglycerin.

In order to determine the lowering effect of the dinitrate on the freezing point of nitroglycerin, a form of apparatus was adopted similar to that used by Kast (*loc. cit.*) for determining the melting points of the nitroglycerin isomerides, and by Hibbert (*Eighth International Congress of Applied Chemistry*, 1912, IV, 37).

About 5 c.c. of the mixture were inserted in a test-tube (15 × 1 cm.) which was fitted into a slightly larger tube, whereby the glyceryl nitrates were protected by an air-jacket from the too rapid action of the freezing mixture. The freezing agent consisted of ice where mixtures of higher melting point were concerned, and of ice and salt for those of lower melting point. The thermometer was allowed to stand in the mixture, direct contact between glass and glass being prevented by enclosing the lower portion of the thermometer bulb in a band of elastic. The stirrer consisted of a flexible piece of platinum wire which was attached to a weighted string wound over a simple pulley, and fastened at

the further end to the outer edge of a wooden disk rotated by a motor. The liquid was first supercooled to the extent of about 4° or 5°. It was then inoculated with a small quantity of a frozen mixture of nitroglycerin, wood-pulp, and sodium nitrate, and vigorously stirred. The maximum temperature was then carefully noted and taken as the freezing point. It will be seen that the values found for the molecular depression constant for nitroglycerin vary from 72·4 to 81·0, thus differing not very greatly from those obtained by Nauckhoff (*loc. cit.*) and by Kast (*loc. cit.*) with ethyl nitrate and monochlorohydrin dinitrate respectively. These numbers are in fair agreement with the value 70·5 for the freezing-point constant for nitroglycerin obtained by Nauckhoff (*loc. cit.*) from a determination of its latent heat of fusion. Nauckhoff's method was, however, admittedly defective, and his results differ very considerably from those of Hibbert and Fuller (*loc. cit.*), who found the latent heat of fusion (h) of nitroglycerin at 0° to be 33·2 calories. Corrected to 13°, the melting point of stable nitroglycerin, this would become $33·2 + 13·0 \ (c_1 - c_2)$, where c_1 and c_2 are the specific heats of solid and liquid nitroglycerin respectively. Accepting Nauckhoff's values of 0·356 and 0·315 for these, the latent heat of fusion of nitroglycerin at 13° would be $33·2 + 13·0 \ (0·356 - 0·315) = 34·33$.

Hence the freezing-point constant

$$\frac{RT^2}{100h} = \frac{0·1991 \times (273 + 13)^2}{100 \times 34·33} = 48·5.$$

The results are set forth in the following table, which includes Nauckhoff's and Kast's values derived from ethyl nitrate and chlorohydrin dinitrate:

Composition of liquid.		Depression of freezing point. (Δ)	Molecular depression constant.	
Nitro-glycerin. Grams.	Methylin dinitrate. Grams.		Calculated from Δ	Calculated from latent heat (Hibbert and Fuller).
31·69	1·802	2·1°	72·4	48·5
15·31	1·748	4·4	75·6	,,
8·22	1·729	8·7	81·0	,,
	Chloro-hydrin dinitrate.			
21	2·1	4·4	88·4	,,
21	4·2	6·4–7·2	62·7–70·5	
21	6·3	9·4	60·7	
	Ethyl nitrate.		74·1	
			76·0	

Attempts to obtain a labile form of the substance analogous to that of nitroglycerin were made. The liquid was mixed with glass wool and supercooled to varying degrees, with continual stirring with a glass rod. When some of the supercooled liquid which had not been previously frozen was inoculated with a trace of this product, the solid obtained invariably crystallised at 24°.