331. *Some Physical Properties of Tetranitromethane.*

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It has been shown that the method normally used for the preparation of tetranitromethane yields a very impure product. New values are given for the freezing point, refractive index, density, and vapour pressure of tetranitromethane. The absorption spectrum of the vapour has been photographed.

THE generally accepted view of the structure of tetranitromethane has been that it is a symmetrical molecule consisting of four true " nitro-"groups arranged tetrahedrally around a central carbon atom. From time to time it has been argued that one of these groups is different from the other three. Several studies of physical properties of tetranitromethane have aimed at deciding between these possibilities. However, there is no general agreement on the physical constants of the pure substance. Sometimes the method of preparation was not indicated. Where methods and constants are given, the freezing points and refractive indices variously quoted differ widely. The preparation and purification of tetranitromethane are discussed below, and new values are given for some physical constants which are compared with those obtained by previous workers.

EXPERIMENTAL.

Chattaway's convenient preparation (*J.*, 1910, **97**, 2099) gave a product so impure (f. p. 10·5—13·0°) that a prohibitive number of fractional distillations were required to yield reasonable purity. Liang's modification of Chattaway's method (*Org. Syntheses*, 1941, **21**, 105) gives a much purer product (f. p. 13·0—13·5°), the essential purifying step being steam-distillation. Since the residual solution becomes bright yellow during the distillation, the impurity removed by this process may be trinitromethane. After steam-distillation the tetranitromethane was dried (Na_2SO_4) and fractionated, at low pressures, in a micro-still (cf. Schrader and Ritzer, *Ind. Eng. Chem.*, *Anal. Edn.*, 1939, **11**, 54). The column was packed with Fenske rings and reflux was obtained by means of a cold pencil. At 28 mm. a small fraction (probably water) distilled at *ca.* 30°; and the remainder, b. p. *ca.* 42°, was divided into five fractions. The distillation was then repeated using fractions 3, 4, and 5, and although in the second distillation all the fractions distilled within 0·3° fractions 1, 2, and 6 were again discarded. The tetranitromethane from this distillation was then distilled into an all-glass apparatus from room temperature to liquid-air temperature across phosphoric oxide. The phosphoric oxide tube was then sealed off and the liquid finally divided into five fractions by vacuum-distillation to liquid-air temperatures. Fractions 1 and 5 were discarded; fraction 3 was used on the apparatus, and small fractions 2 and 4 were used for measurements of physical properties. The values for fractions 2 and 4 were always identical. Four separate batches of tetranitromethane were submitted to this complete purification and all finally gave the same m. p. and refractive index. The liquid obtained always had a faint yellow colour when viewed in fair thickness. Some workers have claimed that the pure substance is colourless.

Freezing Point.—F. p.s were measured by plotting cooling curves for the liquid. The thermometer was read to 0·1° and was calibrated to this accuracy against a N.P.L.-standardised thermometer.

Refractive Index.—The refractive Index was measured with an Abbé refractometer (Hilger), read to 0·0002 unit and compensated to give the refractive index for the Na_D line. Temperatures were ±0·2°, and the instrument was calibrated with a glass sample supplied by the manufacturers and with distilled water.

Density.—Densities were measured with a pyknometer calibrated with distilled water. Only 1-ml. samples of the purest tetranitromethane were available, so the densities are accurate only to about 1 part in 5000. Temperatures were controlled to 0·1°.

Vapour Pressure.—Some measurements of vapour pressure were made at room temperatures in an all-glass system with a Bourdon spoon gauge. Tetranitromethane vapour attacks tap grease so rapidly that reliable measurements cannot be made even in the presence of only one greased tap. These vapour-pressure measurements, together with the b. p.s found around 40° during various fractional distillations, gave a good straight line on a conventional plot of the logarithm of the vapour pressure against the reciprocal of the absolute temperature. The straight line could be represented by $\log_{10} p(\text{mm. Hg.}) = 8{\cdot}63 - 2260/T(^\circ\text{K.})$, and extrapolates to give reasonable agreement with Menzies's vapour-pressure measurements (*J. Amer. Chem. Soc.*, 1919, **41**, 1336) at higher temperatures. From this equation the latent heat of vaporisation was calculated as 10·3 kcals./g.-mol. Smoothed values for the vapour pressure are :

° c.	0	13·8	20	30	40
V. p., mm. (Hg)	1·9	5·7	8·4	14·9	25·8

Absorption Spectrum.—The absorption spectrum of tetranitromethane vapour was photographed using a Hilger spectrograph (medium quartz type E3). With a path length of 1 metre and a pressure of 7 mm., absorption starts at 3050 A., increases to a max. at 2750 A., decreases to a min. at 2500 A., and becomes continuous below 2400 A. No trace of a banded structure was observed.

Explosion Risk.—Because of the reputed explosion risk (Liang, *loc. cit.*; Macbeth, *Ber.*, 1913, **46**, 2537), tetranitromethane was handled only in small quantities. The material used in the present work did not detonate when hammered between steel surfaces. If a small quantity of benzene was added, this treatment caused a violent detonation. It is unwise to dogmatise over questions of explosive sensitivity but it seems probable that pure tetranitromethane is a comparatively insensitive explosive as far as impact shock is concerned, but that it becomes very sensitive when contaminated with aromatic substances or alkali (cf. Bowden, Mulcahy, Vines, and Yoffe, *Proc. Roy. Soc.*, 1947, **188**, *A*, 291). Steam-distillation seems a safe process. No change in properties occurred when tetranitromethane was kept in glass vessels at room temperature for several weeks. At room temperatures the vapour attacks tap grease, rapidly giving off gaseous decomposition products, and also attacks mercury. Thus "vacuum-stability tests" of the type described by Farmer (*J.*, 1920, **117**, 1432), carried out at high temperatures in the presence of both mercury and grease, greatly exaggerate the "instability" of the liquid.

The table below collects values of physical constants given by us and others. Other authors quote a wide range of freezing points, none, however, higher than 13·5°. For ease of comparison some corrections have been applied as set out in the footnotes below the table.

		Density (g./ml.).			n_D.	
Ref.	F. p., °c.	15°.	20°.	25°.	20°.	25°.
1	—	(*a*) 1·6446	—	1·6336	1·4382	1·4359
		(*b*) 1·648	—	1·631	—	—
2	13·75	1·650	—	—	—	—
3	13·0	1·646	—	—	1·4383	—
4	12·5—13·5	—	1·638	1·629	—	—
5	11·5—12·5	—	—	—	—	—
6	—	—	—	1·62294	—	1·43822
7	13·8	1·649	—	1·630	1·4384	1·4358

[1] von Auwers and Ottens, *Ber.*, 1924, **57**, 447, and von Auwers and Herres, *Ber.*, 1929, **62**, 2287. The refractive indices are interpolated from their figures for the hydrogen lines at different temperatures. The density values (*a*) and (*b*) are calculated from their values at 16·9° and 21·2°, the author's value for the temperature coefficient of density being used for (*b*).

[2] Orton and McKie, *J.*, 1920, **117**, 283. Density calculated from their specific gravity at 15·8° using the author's value for the temperature coefficient.

[3] Pictet and Genequand, *Ber.*, 1903, **36**, 2225. Calculated using the author's temperature coefficients.

[4] Hammick and Young, *J.*, 1934, 32; 1936, 1463.

[5] Coop and Sutton, *J.*, 1938, 1269. F. p. measured before one fractional distillation.

[6] Lewis and Smyth, *J. Amer. Chem. Soc.*, 1939, **61**, 3067.

[7] This work.

DISCUSSION.

The tetranitromethane used in the present work was more carefully fractionated than that used by other workers and had the highest recorded freezing point; its vapour pressure, refractive index, and density agree well with the most concordant recorded values. The values here recorded are claimed as more reliable than those previously accepted.

Mark and Noethling (*Z. Kryst.*, 1927, **65**, 435) suggested, from a Debye–Scherrer study of crystalline tetranitromethane, that one of the nitro-groups has a nitrite structure. This view receives no support from the absorption spectrum of the vapour; for the spectrum is almost identical with that described by Hirschlaff and Norrish (*J.*, 1936, 1580) and Thompson and Purkis (*Trans. Faraday Soc.*, 1936, **32**, 674) for nitromethane and shows no trace of the banded structure found by the latter authors for the alkyl nitrites. Coop and Sutton (*loc. cit.*) and Lewis and Smyth (*loc. cit.*) measured the dipole moment of tetranitromethane and obtained values different from zero, although in both papers it was considered that the difference could be accounted within the experimental error of their methods; their tetranitromethane was prepared by Chattaway's method and purified by one distillation; since these materials were far from pure (cf. table), the impurity might suffice to explain the dipole-moment results. Most of the more recent physicochemical work of Médard (*J. Chim. physique*, **1935**, **32**, 136) and Mathieu and Massignon (*Compt. rend.*, 1940, **211**, 323) on infra-red and Raman spectra, and of Stosick (*J. Amer. Chem. Soc.*, 1939, **61**, 1127) on electron diffraction, favours the symmetrical structure with four true " nitro-"groups.

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