VAPOR PRESSURES AND CRYOSCOPIC DATA FOR SOME ALIPHATIC DINITROXY AND TRINITROXY COMPOUNDS

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Vapor pressures of nine aliphatic dinitroxy and trinitroxy compounds were determined at 20, 30 and 40° by use of the transportation method. Heats of vaporization were calculated by means of the Clausius–Clapeyron equation. Freezing curves on 0.2 to 0.5 g. samples were used to determine purity, heats of fusion and freezing points for zero impurity for six compounds which froze at an appreciable rate. Refractive indices of the liquids are given.

Introduction

As a part of a series of studies of physical properties of compounds containing explosive groups, vapor pressures were determined at 20, 30 and 40° for six aliphatic dinitroxy and three aliphatic trinitroxy compounds by means of a transpiration method. Heats of vaporization were calculated by means of the Clausius–Clapeyron equation.

Freezing curve techniques, modified for use with small amounts of explosive material, were used to determine purity, heats of fusion and freezing points corrected to zero impurity. This technique was applicable to six compounds which froze at an appreciable rate.

Experimental

Materials Used.—1,3-Dinitroxypropane, nitroglycerin I, nitroglycerin II, 1,3-dinitroxybutane, 1,4-dinitroxybutane, 1,2,4-trinitroxybutane, 1,5-dinitroxypentane, 2,4-dinitroxypentane, 1,2,5-trinitroxypentane and 2,5-dinitroxyhexane were prepared and purified by Louis Silberman.[2] Nitroglycerin I was prepared by nitrating glycerol with sulfuric acid and nitric acid; nitroglycerin II was prepared by use of nitric acid alone in the nitration. The remaining compounds were prepared by mixed acid nitration of the alcohols. After purification by repeated washings, distillations and crystallizations the compounds were dried in an Abderhalden drier (boiling methylene chloride and phosphoric anhydride) and aerated for 24 to 48 hours with dry metered air to a constant rate of loss in weight.

Methods Used for Freezing Points, Purity and Heats of Fusion.—The freezing curve apparatus is arranged in a manner similar to that of Glasgow, Streiff and Rossini.[3] The sample tube and cryostat were reduced to a size more suitable for use with samples of from 0.2 to 0.5 g. Temperature measurements were made with a No. 36 gage copper–constantan thermocouple in conjunction with a Leeds and Northrup K-2 potentiometer and a high sensitivity mirror type galvanometer. The thermocouple was calibrated from a deviation curve for the region below 0° by the determination of the e.m.f.'s at the freezing point of mercury (−38.87°) and the normal sublimation point of carbon dioxide (−78.51°), and drawing a line through the points and the origin (0°). An accuracy better than +2 μv. may be obtained in this manner. Using an equation of the Antoine type, $\log_{10} p = B - A/t + c$ $(c = 273.16)$, the temperature of the carbon dioxide was computed from the equation

$$\log_{10} p = 9.81137 \frac{-1349}{t + 273.16}$$

where the constants were obtained from the data of Myers and Van Dusen.[4]

For the region above 0°, the thermocouple was calibrated at the boiling point of water the melting point of methylnaphthalene (33.62°) and naphthalene (79.81°) previously compared with a platinum resistance thermometer at these points.

The freezing points were determined and the heats of fusion and purity were calculated from the time–temperature freezing curves according to the method first described by White[5] as modified by Schwab and Wichers.[6]

The purity was calculated from the relationship

$$\frac{x}{\Delta T_x} = \frac{x + a}{\Delta T_{x+a}}$$

in which x is the mole fraction of minor component, a is the mole fraction of added impurity, and ΔT_x and ΔT_{x+a} represent the decrease in temperature between two timed corresponding stages of freezing for the sample and the sample plus added impurity, respectively. In the determination of purity by this method, it is essential that the conditions of freezing including the rate of freezing be substantially reproduced between the sample and the sample plus the added impurity. The nitroxyesters were added to each other as impurities.

The heats of fusion and freezing point for zero impurity were calculated in the manner

$$-\ln(1 - x) = \frac{\Delta H_{f_0}(T_0 - T_1)}{RT^2_{f_0}} = \frac{\Delta H_{f_0}T_0}{RT^2_{f_0}} - \frac{\Delta H_{f_0}T_1}{RT^2_{f_0}} \quad (1)$$

$$-\ln(1 - x - a) = \frac{\Delta H_{f_0}(T_0 - T^*)}{RT^2_0} = \frac{\Delta H_{f_0}T_0}{RT^2_0} - \frac{\Delta H_{f_0}T^*}{RT^2_0} \quad (2)$$

Subtracting eq. 2 from eq. 1

$$\ln\frac{(1 - x - a)}{(1 - x)} = \frac{\Delta H_{f_0}T^*}{RT^2_0} - \frac{\Delta H_{f_0}T_1}{RT^2_0} = \frac{\Delta H_{f_0}(T^* - T_1)}{RT^2_0} \quad (3)$$

then

$$\frac{\Delta H_{f_0}}{T^2_0} = \frac{R}{(T^* - T_1)} \ln\frac{(1 - x - a)}{(1 - x)} \quad (4)$$

but from eq. 1

$$\frac{\Delta H_{f_0}}{T^2_0} = \frac{-R\ln(1 - x)}{(T_0 - T_1)} \quad (5)$$

T_0, T_1 and T^* are the freezing points of the pure substance, the substance with x mole fraction of impurity and with $x + a$ mole fraction of impurity, respectively.

The quantity $\Delta H_{f_0}/T^2_0$ was calculated from experimental data by eq. 5.

For systems which approach ideal solutions such as benzene–toluene and naphthalene–methylnaphthalene, this procedure was found to give values of x within about 2% of the known values.

Nitrogen determinations by means of a nitrometer were made, and the relation between experimental nitrogen and theoretical nitrogen is included for comparison of the purity determinations.

Method Used in Vapor Pressure Measurements.—The vapor pressures were determined by the transpiration

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[1] Published with permission of the Bureau of Ordnance, Navy Department. The opinions and conclusions are those of the authors.

[2] Picatinny Arsenal, Dover, New Jersey.

[3] A. R. Glasgow, Jr., A. J. Streiff and F. D. Rossini, *J. Research Natl. Bur. Standards*, **25**, 355 (1945).

[4] C. H. Myers and M. S. Van Dusen, *J. Research Natl. Bur. of Standards*, **10**, 381 (1933). R.P. 538 (See also reference No. 6, p. 212).

[5] W. P. White, THIS JOURNAL, **24**, 292 (1920).

[6] "Temperature, Its Measurement and Control in Science and in Industry," Reinhold Publishing Corp., New York, N. Y., 1941, p. 256.

TABLE I

FREEZING POINTS, PURITY ESTIMATES AND HEATS OF FUSION OF SELECTED NITRATE ESTERS

		% Nitrogen based on				Heats of fusion	
Compound	Cor. f.p. (°C.)	Theory	Nitrometer	% theor. nitrogen	Mole % purity by freezing curves	Cal./g.	Kcal./mole
1,3-Dinitroxypropane	−29.49	16.87	16.82	99.70	>97 (est.)	..	..
Nitroglycerin (mixed acid nitration)	12.83	18.51	18.47	99.78	99.71	25.0	5.68
Nitroglycerin (straight acid nitration)	12.86	18.51	18.48	99.84	100.00	28.1	6.36
1,3-Dinitroxybutane	−19.78	15.55	15.55	100.00	99.81	22.2	4.00
1,4-Dinitroxybutane	12.3	15.55	15.55	100.00	99.98	35.4	6.38
1,2,4-Trinitroxybutane	−11.34	17.43	17.42	99.94	>97 (est.)	..	...
1,5-Dinitroxypentane	−16.59	14.43	14.41	99.86	99.69	19.1	3.70
2,4-Dinitroxypentane	−18.48	14.43	14.38	99.65	99.81	29.8	5.79
1,2,5-Trinitroxypentane	...	16.47	16.46	99.94	....	..	...
2,5-Dinitroxyhexane	50.37	13.46	13.38	99.41	99.68	63.4	13.2

method as used by Crater[7] and modified by Brandner.[8] The measured amount of dry air passed through liquid samples contained in two absorption bulbs by siphoning water from a calibrated 50-liter container and the loss in weight of the sample was determined on a semi-micro balance. The solid was contained in long narrow tubes with sintered-glass discs to prevent mechanical loss of the sample. A mercury manometer near the Geissler bulbs was used to measure the pressure developed due to resistance to flow of the air passing through the system. Constant temperature was maintained to ±0.1°. If the change in the weight of the second bulb exceeded 1% of that in the first bulb, the determination was discarded. From 6 to 8 valid determinations in total were made for each compound except for the solid, 2,5-dinitroxyhexane, in which case 20 determinations were made.

Assuming that the ideal gas laws hold and that Dalton's law of partial pressure is applicable, the following expression is used to calculate the vapor pressures

$$P_x = \frac{V_x(H_0 - P_0)}{V_0 + V_x}$$

where

P_x = vapor pressure of sample (mm.)
V_x = vol. of vapor found (ml. S.T.P.)
H_0 = barometer pressure (cor., mm.)
V_0 = vol. of air drawn through (S.T.P.)
P_0 = corrn. for head of liquid in Geissler bulb and resistance to air flow in drying train for the inflowing air

Experimentally, it is assumed that 1 mole of vapor occupies 22,400 ml. and V_x = 22,400 (wt. of material volatilized/mol. wt.) and

$$V_0 = V\frac{(H_0 - p - b)}{760} \times \frac{273}{t + 273}$$

where

p = corrn. to barometric pressure due to head of liquid in bulbs and the resistance to air flow of drying trains
b = vapor pressure of water at t°C.
t = final temp. of aspirator °C.
V = vol. of water run out of aspirator in ml.

The heats of vaporization were computed by a least squares treatment of the vapor pressures at the three temperatures using the Clausius–Clapeyron equation. The procedure was as follows[9]

$$E = \Sigma(\ln p)^2 - \frac{\Sigma(\ln p^2)}{n} - b^2\left(\Sigma\left(\frac{1}{T}\right)^2 - \frac{(\Sigma 1/T)^2}{n}\right)$$

where E is the sum of the squares of the deviations of ln p from the least squares equation of slope b, and n is the number of measurements. The variance of the slope was computed from

$$\sigma^2 = \frac{\dfrac{E}{n-2}}{\Sigma\left(\dfrac{1}{T}\right)^2 - \dfrac{(\Sigma 1/T)^2}{n}}$$

and the appropriate coefficient for a 95% confidence interval was then applied.

Results and Discussions

Freezing Curve Results.—Table I presents the freezing points corrected to zero impurity, the purity as determined from freezing curves, the per cent. theoretical nitrogen measured and the heats of fusion. 1,3-Dinitroxypropane and 1,2,4-trinitroxybutane could be made to freeze but at a very slow rate. For 1,2,4-trinitroxybutane a freezing point could also be obtained between 9 and 10°. This is analogous to the two forms of nitroglycerin which freeze at 12.86 and 1.9–2.2°.[10]

The 1,2,5-trinitroxypentane could not be made to freeze but the nitrogen analysis is included because the vapor pressure was determined for that sample.

Because the purity determinations by freezing curves are more reliable than those by the nitrometer for small quantities of impurity, a comparison with the nitrometer determinations is of interest. A comparison with the results of the two methods for 1,4-dinitroxybutane and nitroglycerin II, 99.98 and 100.00 mole % pure, respectively, would eliminate ambiguity due to possible nitrate impurities. In these cases the nitrometer is 0.02% high and 0.16% low, respectively. These results are within the precision (about 2 parts in 1500) obtained with the potassium nitrate used in calibration. The heats of fusion for the two nitroglycerin samples, are 5.68 and 6.38 kcal./mole, respectively. It is not believed that this difference is due to difference in mole % purity as determined by freezing curve methods but indicates uncertainty that might be expected in applying these semi-micro methods to the determination of purity. Small errors in the freezing point depression could cause large errors in the heat of fusion.

Vapor Pressure Results.—The vapor pressure results are given in Table II. The vapor pressures of nitroglycerin agree reasonably well with those obtained by Marshall and Peace[11] and with those obtained by Ernsberger, *et al.*[12]

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[7] W. C. Crater, *Ind. Eng. Chem.*, **21**, 674 (1929).

[8] J. D. Brandner, *Ind. Eng. Chem.*, **30**, 681 (1938).

[9] C. A. Bennett and N. L. Franklin, "Statistical Analysis in Chemistry and Chemical Industry," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 38.

[10] T. L. Davis, "Chemistry of Powder and Explosives," John Wiley and Sons, Inc., New York, N. Y., 1943, p. 207.

[11] A. Marshall and G. Peace, *J. Chem. Soc.*, **109**, 298 (1916).

[12] U. S. Naval Ordnance Test Station; NAVORD Report No. 1184 Part I, by F. M. Ernsberger, J. G. Wyllie and A. L. Olsen, Sept. 28, 1949.

TABLE II

VAPOR PRESSURES AND HEATS OF VAPORIZATION OF SELECTED NITRATE ESTERS

Compound	Vapor pressure (μ) 20°	30°	40°	Heat of vaporization (kcal./mole)
1,3-Dinitroxypropane	17, 16	41, 42	118, 114, 116	17.9 ± 1.1
Nitroglycerin I	0.21, 0.23, 0.18	0.82, 0.82, 0.80	3.4, 3.3, 3.0	25.1 ± 1.4
Nitroglycerin II	0.20, 0.20	1.0, 1.1, 1.2	3.8, 3.5, 3.4	26.0 ± 2.7
1,3-Dinitroxybutane	23, 21	50, 52	142, 137, 151	17.2 ± 1.7
1,4-Dinitroxybutane	9.1	20, 20, 20	41, 41	13.7 ± 0.2
1,2,4-Trinitroxybutane	1.2, 1.0	2.8, 2.2	5.2, 5.4	14.4 ± 2.7
1,5-Dinitroxypentane	4.3, 5	14.1, 13.3	36.8, 36.2	18.8 ± 1.4
2,4-Dinitroxypentane	30, 27, 30	73, 71	143, 137	14.5 ± 1.4
1,2,5-Trinitroxypentane	0.16	0.27, 0.30, 0.29	0.46, 0.50	10.0 ± 0.5
2,5-Dinitroxyhexane	0.98, 1.23, 1.33	6.1, 7.2, 7.6	24, 27, 26	26.2 ± 3.8[a]
	1.28	9.4, 7.4, 7.0	28, 28, 37	(13.0)[b]
		8.7, 7.4	25, 31, 19	

[a] Heat of sublimation. [b] Heat of vaporization computed by subtracting heat of fusion.

Marshall and Peace obtained the vapor pressure of nitroglycerin by air saturation techniques. The air was passed through ground cordite. (Composition: guncotton 37, mineral jelly 5, nitroglycerin 58.) The ground surface of the cordite served as saturators. Ernsberger, *et al.*, obtained their values with a modification of Knudsen's effusion cell.

The heat of vaporization of nitroglycerin is considerably higher than those of the other compounds. The viscosity of nitroglycerin and also the rate of change of viscosity with temperature have been reported to be considerably higher than for 1,3-dinitroxypropane, 1,3-dinitroxybutane and 1,4-dinitroxybutane.[13-15]

This would be consistent with a higher heat of vaporization for nitroglycerin.

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(14) L. J. De Kreuk, *Rec. trav. chim.*, **61**, 819 (1942).

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X-RAY STUDIES ON THE FORMATION OF COPPER–NICKEL ALLOYS FROM THE PRECIPITATED BASIC CARBONATES

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The formation of copper–nickel alloys by the low temperature reduction of the mixed oxides with hydrogen has been studied. It has been shown that even when two oxidic phases are present, on reduction a single metallic phase is formed in which compositional variations, if present at all, cannot exceed 3%. The oxidic phases formed by the method used in this study appear to be pure CuO and an NiO phase in which up to 35% of the Ni atoms have been substituted by Cu.

A number of years ago, Long, Fraser and Ott[2] demonstrated that the copper–nickel (and a number of other) alloy systems could be formed beginning with the coprecipitation of the metals as the hydroxide from solutions of the mixed ions; these were then reduced to metal with hydrogen. The measured lattice parameters were found to be identical with those determined for the corresponding alloys prepared by melting the metals together. The correctness of this work was confirmed by several other workers[3,4] and has been verified again in the present study.

The reason for the effectiveness of the alloying process just described is not immediately apparent. Although a random distribution of metal atoms is to be expected in the freshly precipitated basic carbonates, subsequent conversion to the oxides by means of thermal treatment should result in segregation of the CuO and NiO crystallites because of their different crystal systems, *viz.*, monoclinic and cubic, respectively. Furthermore, segregation should persist when the oxides are then reduced at relatively low temperatures (200 to 450°) because the inter-diffusion of copper and nickel among adjacent pure crystallites would be expected to be too slow at such low temperatures to produce a significant amount of solid solution. Thus homogeneous alloy systems would not be anticipated on the basis of the foregoing arguments. With these considerations in mind, it was decided to repeat once again this alloying procedure over a wide range of composition, examining both the oxide and alloy phases by X-ray diffraction.

Preparation of the samples of the basic carbonates followed quite closely the modification of the method of Long, Fraser and Ott[2] used by Best and Russell.[4] Analytical reagent grade reagents including Fisher's nickelous nitrate labeled "Low in cobalt" were used, and the precipitation was carried out using ammonium bicarbonate. Tests on

(1) Department of Chemical Physics, Mellon Institute.

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(4) R. J. Best and W. W. Russell, *ibid.*, **76**, 838 (1954).