Fig. 2.—a_0 values of the B.C.C. (γ) phase as a function of composition at room temperature.

from this cell size is 2.083 Å. as compared with 2.148 Å. for that of the F.C.C. form. This represents a difference of 3% between the radii of the atoms in the two structures, a magnitude in good agreement with that predicted for these.[8]

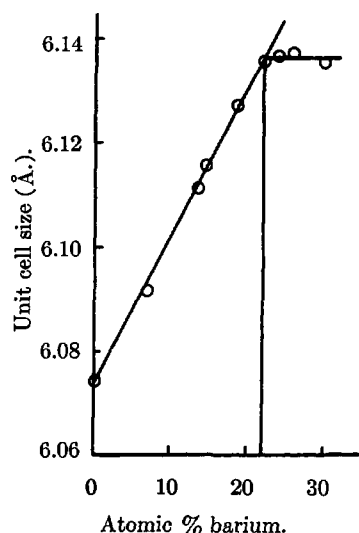(8) L. Pauling, "Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N. Y., 1945, p. 406.

Fig. 3.—a_0 values of the F.C.C. (α) phase as a function of composition at room temperature.

PHYSICAL PROPERTIES OF EIGHT HIGH-PURITY NITROPARAFFINS

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Received August 11, 1955

The boiling point, vapor pressure, freezing point, density and refractive index have been determined for the eight mononitroparaffins from nitromethane through the four isomeric nitrobutanes. The measurements were made on highly purified samples, characterized by both ebullioscopic and cryoscopic methods. The vapor pressure data have been fitted to the Antoine equation by the method of least squares.

Introduction

Physical properties of the mononitroparaffins have been appearing in the literature during the past 80 years. Few reliable data are available, with the exception of nitromethane, whose properties were carefully measured by Timmermans and Hennaut-Roland.[1] Measurements made during the past 20 years are particularly liable to error because commercial products have been used without adequate purification.

Nitromethane, nitroethane and 1- and 2-nitropropane are made commercially by the vapor phase nitration of propane.[2] These materials are available containing 90–95% w. of the specified product with a total nitroparaffin content of at least 99%. A careful fractional distillation is essential to obtain a high purity nitroparaffin. A summary of physical data on these compounds recently has been published.[3]

Whenever possible the nitroparaffins were prepared by synthesis as well as by purifying the commercial product. The primary nitroparaffins can be prepared in good yields from the corresponding

(1) J. Timmermans and M. Hennaut-Roland, *J. chim. phys.*, **29**, 529 (1932).

(2) C. L. Gabriel, *Ind. Eng. Chem.*, **32**, 887 (1940); S. D. Kirkpatrick, *Chem. & Met. Eng.*, **49**, [9], 129 (1942).

(3) A. Weissberger, "Technique of Organic Chemistry," Vol. VII, Interscience Publishers, Inc., New York, N. Y., 1955.

alkyl bromide or iodide by the Victor Meyer reaction.[4] They may also be prepared in satisfactory yields from the corresponding α-halogenated acid by the Kolbe synthesis.[5] This method is an excellent laboratory preparation of nitromethane from chloroacetic acid.[6]

All purifications of both the synthetic and commercial nitroparaffins were made by careful fractional distillation, except for nitromethane where both fractional distillation and fractional crystallization were used. The products were collected in 100-ml. fractions during the distillation and preliminary purity measurements made by mass spectra analysis.

Preparation and Purification of the Nitroparaffins

Nitromethane was prepared from the commercial product by fractional distillation in a Podbielniak Hyer-Cal column at 100 mm. pressure, followed by a fractional crystallization in which one-half of the sample was discarded as mother liquor. A material of equivalent purity was prepared from chloroacetic acid and sodium nitrite.

(4) V. Meyer, *Ber.*, **5**, 203, 399, 514, 1029, 1034 (1872); N. Kornblum, N. Lichtin, *et al.*, *J. Am. Chem. Soc.*, **69**, 307 (1947); N. Kornblum, J. T. Patton and J. B. Nordmann, *ibid.*, **70**, 746 (1948); C. W. Plummer and N. L. Drake, *ibid.*, **76**, 2720 (1954).

(5) H. Kolbe, *J. prakt. Chem.*, **5**, 427 (1872); W. Steinkopf and G. Kirchhoff, *Ber.*, **42**, 3438 (1909); A. Wahl, *Bull. soc. chim.*, **5**, 180 (1909).

(6) H. Gilman and A. H. Blatt, "Organic Syntheses," Coll. Vol. I. John Wiley and Sons, Inc., New York, N. Y., 1941, p. 401.

Nitroethane was prepared by the Victor Meyer reaction from purified bromoethane. Purification was done in a 30 plate Penn State-type column at 100 mm. pressure. It was not possible to prepare nitroethane of a purity greater than 99.8% mole by fractional distillation of the commercial product.

1-Nitropropane was prepared by both the Victor Meyer reaction and fractional distillation of the commercial product in a 60 plate Penn State-type column at 100 mm. pressure. A reflux ratio of 75:1 was used. Both methods gave material of equal purity.

2-Nitropropane was prepared by fractional distillation of commercial material in the same manner as 1-nitropropane.

1-Nitrobutane, prepared by nitrating butane, was fractionally distilled in a Podbielniak Hyer-Cal column at 100 mm. pressure using a 100:1 reflux ratio. Its purity was equivalent to material prepared by the Victor Meyer reaction.

2-Nitrobutane was prepared and purified by the same procedure as 1-nitrobutane.

1-Nitro-2-methylpropane was prepared from 1-bromo-2-methylpropane by the Victor Meyer reaction. The yield was low and purification was difficult. Two fractional distillations in 30 plate Penn State-type columns at 50 mm. pressure and a redistillation in a Podbielniak Hyer-Cal column were required to obtain a product of acceptable purity.

2-Nitro-2-methylpropane was prepared from t-butylamine by the method of Kornblum and Clutter.[7] The crude product was dried with Drierite overnight and fractionally distilled in a 30 plate Penn State column at atmospheric pressure.

Experimental

All temperature measurements were made with platinum resistance thermometers connected to a Leeds and Northrup type G-2 Mueller bridge through a mercury switch of negligible resistance. The thermometers were compared against one calibrated by the National Bureau of Standards. Measurements were made to ±0.001° but in this paper have been rounded off to the nearest 0.01°.

Purity measurements were made by both cryoscopic[8] and ebullioscopic methods.[9] The cryoscopic and ebullioscopic purities are tabulated in Table I. The Roman numerals are the Swietoslawski purity class[9] and Δt is the difference between the boiling point of the liquid and the condensing temperature of the vapor.

TABLE I
PURITY OF THE NITROPARAFFINS

	From freezing curve, mole %	Purity From boiling point Class	Δt, °C.
Compound			
Nitromethane	99.99	IV	0.007
Nitroethane	99.9+	IV	.013
1-Nitropropane	99.9+	IV	.007
2-Nitropropane	99.99	III	.046
1-Nitrobutane	99.96	III	.022
2-Nitrobutane	Indeterminable	III	.023
1-Nitro-2-methylpropane	99.82	III	.021
2-Nitro-2-methylpropane	Indeterminable	IV	.008

The freezing points are tabulated in Table II. Calculated values for zero impurity are given for nitromethane, 2-nitropropane, 1-nitrobutane and 1-nitro-2-methylpropane. The freezing points of the other nitroparaffins are experimental values since exact calculations could not be made.

The boiling points, degree of purity and vapor pressure were measured in Swietoslawski differential ebulliometers. The ebulliometers were constructed from the improved

(7) N. Kornblum and R. J. Clutter, *J. Am. Chem. Soc.*, **76**, 4494 (1954).

(8) B. J. Mair, A. R. Glasgow and F. D. Rossini, *J. Research Natl. Bur. Standards*, **26**, 591 (1941).

(9) W. Swietoslawski, "Ebulliometric Measurements," Reinhold Publ. Corp., New York, N. Y., 1945, p. 80.

TABLE II
FREEZING POINTS OF THE NITROPARAFFINS

Compound	Freezing point, °C.
Nitromethane	− 28.55
Nitroethane	− 89.52
1-Nitropropane	−103.99
2-Nitropropane	− 91.32
1-Nitrobutane	− 81.33
2-Nitrobutane	Glass
1-Nitro-2-methylpropane	− 76.85
2-Nitro-2-methylpropane	26.23

Swietoslawski design, adapted to electrical heating.[10] The original design was followed except for decreasing the diameter of the thermometer well to better accommodate the Leeds and Northrup Type 8160 resistance thermometers.

The vapor pressures were measured in two Swietoslawski ebulliometers connected to a five-gallon reservoir following the arrangement of Smith and Matheson.[11] A vacuum pump and open end manometer were connected to the reservoir. The nitroparaffin was placed in one ebulliometer and water, distilled from an alkaline permanganate solution, placed in the other. The two ebulliometers were separated by a cold trap. The ebulliometers were evacuated to approximately the lowest pressure desired and simultaneous measurements made of the boiling points of the nitroparaffin and water. Dry air was then bled into the system to raise the pressure and the boiling points again measured. This procedure was repeated until the desired number of points had been obtained. Fifteen to twenty observations were made on each compound starting at about 80 mm.

The experimental vapor pressure data consisted of the boiling points of the nitroparaffin and water for each individual pressure in terms of ohms. After correcting for lead resistance, bridge zero and individual resistance errors they were converted to temperature by use of the Callendar formula. The pressure for each point was then calculated from the boiling point of water, using the data of Osborne and Meyers.[12] The data were fitted to the Antoine equation by the method of least squares.

The boiling points at 760 mm. were calculated from the vapor pressure equation and are tabulated in Table III, together with the pressure coefficients of temperature. The Antoine constants are given in Table IV. The average deviation between the calculated and experimental pressure ranged from ±0.03 mm. for nitromethane to ±0.06 mm. for 2-nitrobutane. The maximum deviation was 0.10 mm. for nitromethane and 0.15 mm. for 2-nitrobutane.

TABLE III
BOILING POINTS AND PRESSURE COEFFICIENTS OF TEMPERATURE OF THE NITROPARAFFINS

Compound	B.p., °C. (760 mm.)	dt/dp, °C./mm.
Nitromethane	101.20	0.0427
Nitroethane	114.07	.0445
1-Nitropropane	131.18	.0467
2-Nitropropane	120.25	.0460
1-Nitrobutane	152.77	.0490
2-Nitrobutane	139.50	.0485
1-Nitro-2-methylpropane	141.72	.0482
2-Nitro-2-methylpropane	127.16	.0473

Density measurements were made in a Sprengel-type pycnometer having a capacity of about 17 ml. Calibrations were made with freshly boiled redistilled water. The weighing procedure used was adapted to 5th decimal place accuracy. Measurements were made at 20, 25 and 30° for all compounds except 2-nitro-2-methylpropane. The precision of the measurements was checked by comparing

(10) W. E. Barr and V. J. Anhorn, *Instruments*, **20**, 822 (1947); A. Weissberger, "Technique of Organic Chemistry," Vol. I, pt. 1, Interscience Publishers, Inc., New York, N. Y., 1949, p. 107.

(11) E. R. Smith and H. Matheson, *J. Research Natl. Bur. Standards*, **20**, 641 (1938).

(12) N. S. Osborne and C. H. Meyers, *ibid.*, **13**, 1 (1934).

TABLE IV
CONSTANTS OF THE ANTOINE EQUATION

$$\log p = A - \frac{B}{t + C}$$

Compound	A	B	C
Nitromethane	7.274170	1441.610	226.939
Nitroethane	7.175154	1435.402	220.184
1-Nitropropane	7.127539	1474.299	215.986
2-Nitropropane	7.083240	1422.898	218.341
1-Nitrobutane	7.095500	1523.797	208.778
2-Nitrobutane	7.077892	1494.318	216.542
1-Nitro-2-methyl-propane	7.074141	1483.643	212.095
2-Nitro-2-methyl-propane	6.987722	1396.948	212.989

values of dd/dt calculated between 20 and 25°, 25 and 30° and 20 and 30°. The precision was ±0.00002 g./ml. and the estimated accuracy ±0.00004 g./ml. These data are tabulated in Table V.

TABLE V
DENSITIES OF THE NITROPARAFFINS

Compound	20°	Density 25°	30°	dd/dt
Nitromethane	1.13816	1.13128	1.12439	0.001377
Nitroethane	1.05057	1.04464	1.03870	.001187
1-Nitropropane	1.00144	0.99609	0.99073	.001071
2-Nitropropane	0.98839	.98290	.97740	.001099
1-Nitrobutane	.97344	.96848	.96352	.000992
2-Nitrobutane	.96535	.96036	.95536	.000999
1-Nitro-2-methyl-propane	.96349	.95848	.95347	.001002
2-Nitro-2-methyl-propane	Solid	Solid	.95028[a]	.001128

[a] d^{35}_4 0.94464.

A dipping refractometer was used to measure refractive index. The prisms were calibrated with either distilled water, sodium chloride solutions of known refractive index or fluorite test plates. The precision of measurement, estimated from values of dn/dt, is about ±0.000025 unit with an estimated accuracy of ±0.00005.

Discussion

It was not possible to calculate the cryoscopic purity for 2-nitro-2-methylpropane or 2-nitrobutane. The latter compound did not freeze but became glassy at about −111° while the freezing curve of the former exhibited a plateau in the cooling curve close to the freezing point. This plateau re-

TABLE VI
REFRACTIVE INDICES OF THE NITROPARAFFINS

Compound	20°	Refractive index 25°	30°	dn/dt
Nitromethane	1.38188	1.37964	1.37738	0.000450
Nitroethane	1.39193	1.38973	1.38754	.000439
1-Nitropropane	1.40160	1.39956	1.39755	.000405
2-Nitropropane	1.39439	1.39235	1.39028	.000411
1-Nitrobutane	1.41019	1.40801	1.40593	.000426
2-Nitrobutane	1.40407	1.40189	1.39979	.000428
1-Nitro-2-methyl-propane	1.40642	1.40436	1.40232	.000410
2-Nitro-2-methyl-propane	Solid	Solid	1.39715[a]	.000400

[a] n^{35}_D 1.39515.

sembled an eutectic mixture, though it could also be caused by a transformation to a polymorphic form. The high degree of purity indicated by the ebullioscopic measurements would indicate that polymorphism was occurring. However, replicates of the cooling curve all exhibited the plateau regardless of the cooling rate.

Exact purity calculations could not be made on nitroethane or 1-nitropropane. These compounds gave a sharp freezing curve but one in which equilibrium was never reached. After 45 minutes of freezing the freezing curves were showing a small, steady rise in temperature. However, the sharpness of the freezing curves, together with the ebullioscopic degrees of purity, indicate that these compounds are at least 99.9% mole.

The ebullioscopic purity measurement is sensitive to traces of water. This is apparent from Table I when the ebullioscopic Δt is compared to the mole % purity calculated from the freezing curve. Freshly distilled nitroparaffins all showed a Δt of between 0.04 to 0.06°, even when elaborate precautions were taken to exclude moisture during the distillation. The Δt for nitromethane, nitroethane, 1-nitropropane and 2-nitro-2-methylpropane all dropped to a low value after these compounds were dried with Drierite. Treatment with Drierite was less effective for 2-nitrobutane, 1-nitro-2-methylpropane and 1-nitrobutane. The Δt's for these compounds were only reduced to about 0.02°. 2-Nitropropane decomposed when in contact with Drierite. The Δt rose from about 0.04 to 0.12°.