In these experiments, unfortunately, both the percentage base and the activator concentration were changed so that it is not clear from the data whether the distribution coefficients decrease with decreasing activator concentration or decrease with increasing percentage of base. It seems reasonably certain from additional experiments that the latter alternative represents the situation. The solubility of strontium oxide in strontium chloride has been found to be quite high and its presence in the flux causes a pronounced decrease in the distribution coefficient of the activators. The effect with the different activators increases in the order europium–cerium–samarium. The strontium sulfide and selenide contain small amounts of oxide which dissolve in the flux so that increasing proportions of the base material in the original mixtures give rise to increasing concentrations of oxide in the flux. This leads to smaller distribution coefficients. The results of a systematic study of this phenomenon will be presented in a later publication.

Acknowledgment.—The authors wish to thank Dr. John R. Dunning and various members of the Radiochemical Laboratories at Columbia University for their friendly coöperation. We are particularly indebted to Mrs. Adele Weil for advice on tracer techniques.

Summary

A technique for filtering fused salt solutions at 1000° has been described.

The distribution of small quantities of europium, cerium and samarium between phosphor base materials (strontium sulfide and strontium selenide) and saturated solutions of the bases in the fluxes (strontium chloride and lithium fluoride) has been studied in the neighborhood of 1000° with the aid of radioactive tracers.

BROOKLYN 2, N. Y. RECEIVED JULY 3, 1948

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF PITTSBURGH, AND MELLON INSTITUTE]

Some Physical Properties of Isoquinoline

BY HENRY FREISER[1] AND WILLIAM L. GLOWACKI[2]

This paper is the second in a series[3] describing the work of a program for the determination of physical constants of coal tar bases, sponsored by the Koppers Company.

Purification of Isoquinoline.—Seventeen gallons of commercial isoquinoline (Koppers Company 2° isoquinoline having a freezing point of 23.8°) was subjected to eight successive fractional crystallizations until the final material (about 2 kg.) had a freezing point of 26.6°. Further purification was effected by a careful fractional distillation at atmospheric pressure through the rectifying column previously used.[3] Fifty-eight fractions of 30 ml. each were collected at the rate of 30 ml./hr., and after the first three fractions boiled within 0.1°. It is interesting to note that the distillation separated a high-melting impurity more volatile than isoquinoline. This material was identified as naphthalene and is believed responsible for the difficulty encountered in the purification by crystallization. The distillation cuts were further screened by measuring freezing points. For all of the physical properties determined, those central cuts whose freezing points differed by less than 0.05° were combined to give a material having a freezing point of 26.41 ± 0.02° and an estimated purity of at least 99.5 mole per cent.

Determination of Properties.—The properties reported here were determined using the same apparatus and procedures previously described.[3]

Freezing Point.—The freezing point of pure isoquinoline is estimated at 26.48 ± 0.1°. Quinoline was found to depress the freezing point of isoquinoline by 0.5 ± 0.1° per mole per cent. If the only impurity in the isoquinoline used were quinoline, the material might be as high as 99.8 mole per cent. pure.

Density and Expansion Coefficient.—The density values at every 10° from 30 to 80° were found to be 1.09101, 1.08309, 1.07519, 1.06731, 1.05945, and 1.05143 g./ml. with an average reproducibility of 0.00004 g./ml. The values of the expansion coefficient in this temperature range varied from 0.000722 at 30° to 0.000776 at 80°. Values of the density at high temperatures were determined as follows: 1.03540 at 100°, 1.01547 at 125°, 0.99498 at 150°, 0.97421 at 175°, and 0.95300 g./ml. at 200°, with an average reproducibility of 0.00006 g. per ml. The corresponding expansion coefficient values varied from 0.000765 to 0.000899.

Viscosity.—The results are presented in Table I.

TABLE I

VISCOSITY OF ISOQUINOLINE

Temp., °C.	Viscosity, cp.	Temp., °C.	Viscosity, cp.
30	3.2528	100	1.0230
40	2.6034	125	0.7787
50	2.1323	150	.6217
60	1.7872	175	.5067
70	1.5269	200	.4223
80	1.3223		

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[3] H. Freiser and W. L. Glowacki, THIS JOURNAL, **70**, 2575 (1948).

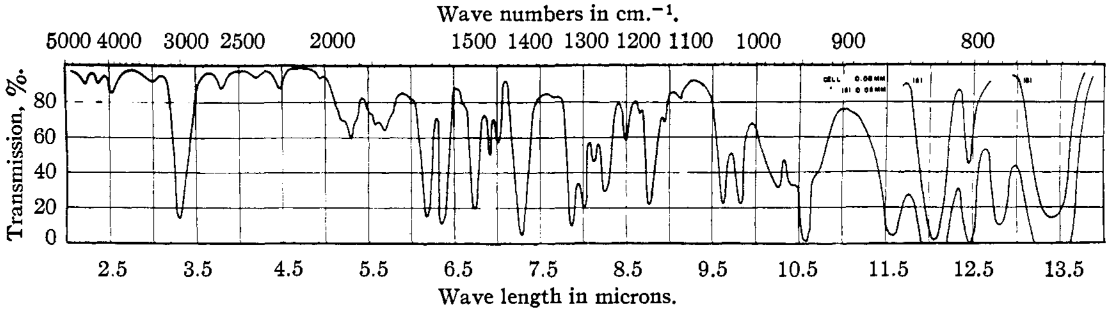

Fig. 1.—Cell, 0.08 mm.; cell 8, 0.04 mm.

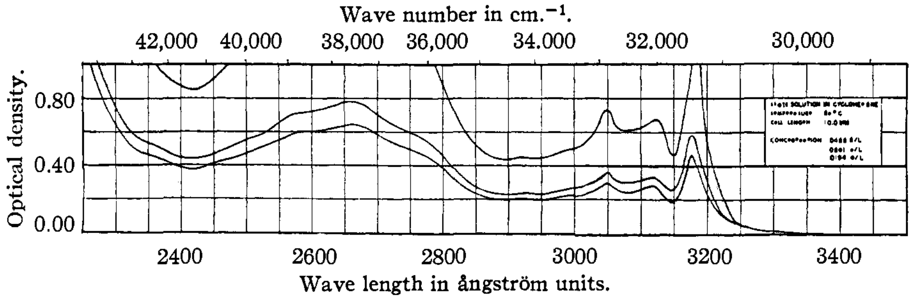

Fig. 2.—State solution in cyclohexane: temperature, 25°; cell length, 10.0 mm.; concn., 0.0482 g./l., 0.0241 g./l., 0.0194 g./l.

Boiling Point.[4]—The boiling points of isoquinoline at various pressures were found to be 242.242° at 743.05 mm., 242.026° at 739.33 mm. and 241.832° at 736.14 mm. These values were determined in a differential Swietoslawski ebulliometer using platinum resistance thermometers certified by the National Bureau of Standards to measure the boiling and condensation temperatures of isoquinoline as well as the boiling point of water in a second ebulliometer to establish the pressure value. A further check on the purity of the isoquinoline was obtained in the small difference, 0.007°, between the boiling and condensation temperatures. The average rate of change of boiling temperature with pressure dT/dp, calculated from the above values, was 0.0594 ± 0.0009° per mm. From this the boiling point at 760 mm. pressure was calculated at 243.25°. Extrapolation of a plot of values of the temperature difference between the boiling points of isoquinoline and water against the pressure to a value at 760 mm. pressure gave the same result. From the values of the boiling point at 760 mm. pressure and that of dT/dp, the heat of vaporization has been calculated by means of the Clausius–Clapeyron equation as 11.7 ± 0.5 kcal. per mole.

Refractive Index.—Values of the refractive index of isoquinoline are n^{30}_{D} 1.62078, $n^{30}_{5461\,\text{Å}}$ 1.62806, and n^{30}_{∞} 1.5799_2 (calcd.).

Dipole Moment.—The dielectric constants ϵ and densities d of the solutions containing mole fraction f_2 of the polar solute and the molar polarization of the solute are given in Table II.

TABLE II

DIELECTRIC POLARIZATION OF ISOQUINOLINE AT 30.0°

f_2	ϵ	d	P_2
0.00000	2.2627	0.868231	(168.1 ± 0.3)
.006112	2.3360	.870837	166.4
.014719	2.3954	.872983	164.5
.025562	2.4930	.876380	162.1
.029533	2.5316	.877705	162.4

The sum of P_{E} and P_{A} was taken to be 43.3 (the value of the molar refraction at infinite wave length plus 10%), giving a value of the dipole moment of isoquinoline of 2.49 ± 0.01 D in fair agreement with previously determined values.[5]

Absorption Spectra.—In Figs. 1 and 2 are presented the infrared and ultraviolet absorption curves, respectively, for isoquinoline. The main infrared absorption maxima are presented in Table III. The main ultraviolet absorption maxima are located at 266, 304, 312, and 318

TABLE III

MAIN INFRARED ABSORPTION MAXIMA OF ISOQUINOLINE

Microns	I^a	Microns	I^a	Microns	I^a	Microns	I^a
3.30	m-i	6.92	w	8.50	w	10.26	m
5.30	w	7.01	w	8.66	w	10.59	i
5.58	w	7.29	i	8.77	m	11.58	i
5.69	w	7.87	i	8.94	w	12.07	i
6.18	m-i	8.01	m	9.14	w	12.46	i
6.35	m-i	8.13	m	9.63	m	12.81	i
6.73	m	8.26	m	9.83	m	13.42	i

[a] Approximate intensity: w = weak, m = moderate, i = intense.

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[4] The help of Dr. John R. Anderson and Mr. Jack Killoran of Mellon Institute with this measurement is gratefully acknowledged.

[5] R. J. W. LeFevre and J. W. Smith, *J. Chem. Soc.*, 2239 (1932).

millimicrons. The data were obtained by the Koppers Spectrographical Research Laboratory at Mellon Institute under the direction of Dr. J. J. McGovern.

Summary

1. Isoquinoline has been purified by fractional distillation and extensive recrystallization to a purity of over 99.5 mole per cent.

2. The following properties have been determined for the purified material: f. p., b. p., density, expansion coefficient and viscosity at frequent temperature intervals between 30 and 200°, refractive index at 5893 and 5461 Å. at 30°, the dipole moment, and the infrared and ultraviolet absorption spectra.

Pittsburgh, Pa. Received July 29, 1948

[Contribution from Project Squid, Purdue Department of Chemistry and School of Chemical Engineering]

1,3-Dinitropropane

By J. P. Kispersky, H. B. Hass and D. E. Holcomb

Introduction

Keppler and Meyer[1] reported 1,3-dinitropropane, prepared by reaction between silver nitrite and 1,3-diiodopropane, to be a yellow, unstable, undistillable oil which changed after several days to a viscous, brown material. On the basis of our present knowledge there seemed to be no adequate reason for expecting 1,3-dinitropropane to be instable. The researches of Kornblum and students[2] in this Laboratory have shown that substantial amounts of organic nitrates are formed in the Victor Meyer reaction and can be removed from the nitro compounds by treatment with sulfuric and phosphoric acids.

3-Nitro-1-propyl nitrate and the corresponding nitrite would be expected to be instable because the primary nitro group tautomerizes to an acidic nitronic acid and neither nitrites nor nitrates are stable to acid.

It, therefore, seemed advisable to repeat the synthesis of 1,3-dinitropropane and to apply the recent purification procedures. As a result, 1,3-dinitropropane has been prepared for the first time in pure form. It is a stable, colorless liquid, distillable at low pressures, b. p. 103° at 1 mm., m. p. −21.4°, molal f. p. const. 4.5, ht. of fusion 27, cal./g., $n^{25}_{\rm D}$ 1.4638, density 1.353 g./ml. at 25.5°, $n_{\rm D}$ 20.0° – 1.4654; 21.6° – 1.4649; 30.0° – 1.4622.

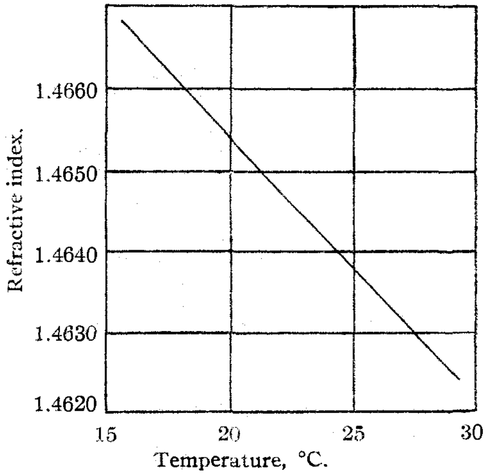

Fig. 1.—Change of refractive index with temperature.

Experimental

The silver nitrite was prepared according to the directions of McElroy.[3] A slurry was formed of five moles (770 g.) of silver nitrite in 1100 ml. of ether and two moles (592 g.) of 1,3-diiodopropane was added with stirring from a dropping funnel. The flask was cooled externally and the rate of addition regulated to cause gentle refluxing of the ether. After the addition was complete, stirring was continued at room temperature in the dark for twenty hours. Afterward the ether solution was removed by decantation and the residue extracted twice with 300 ml. portions of ether, filtered with suction and washed again with 300 ml. of ether. The ether was evaporated over a steam cone, washed with an equal volume of water and dried over Drierite. The orange-colored liquid residue from two such preparations weighed 300 g.

Distillation in a column resulted in decomposition but an ordinary vacuum distillation gave 90 g. of a fraction b. 100–110° at 1 mm. which gave a positive test with diphenylamine in sulfuric acid. Contrary to Mulliken[4] this color test is not given by pure, primary mononitro paraffins.

The material was then added to three times its volume of 96% sulfuric acid at 0°, stirred for several minutes, poured over ice, and the insoluble layer washed with water. After drying with Drierite the 18 g. remaining distilled at 103° at 1 mm. Qualitative tests showed the presence of nitrogen and absence of halogen. The diphenylamine test now showed the absence of nitrite or nitrate ester.

An estimate of the purity of the sample from the freezing point curve showed it to be 98.2 mole per cent. 1,3-dinitropropane. Nitromethane was added as the known impurity.

Analysis by Huffman Microanalytical Laboratories gave the following: Calcd.: H, 4.51; C, 26.87; N, 20.90. Found: H, 4.55, 4.53; C, 26.89, 26.95; N, 21.03, 20.95.

Molar refractivity calculated from Eisenlohr's values is 27.30. Calculated from observed data, 27.33.

Storage of 1,3-dinitropropane at room temperature from September, 1947, to July, 1948, produced no visible alteration.

Summary

1,3-Dinitropropane has been prepared for the first time in a state of high purity and the common physical constants determined.

Received August 6, 1948

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[1] Keppler and Meyer, *Ber.*, **25**, 1710 (1892).

[2] Kornblum, Lichtin, Patton and Iffland, This Journal, **69**, 307 (1947).

[3] W. R. McElroy, Ph.D. Thesis, Purdue University, 1943.

[4] Mulliken, "Identification of Pure Organic Compounds," Vol. II, 1916, p. 28.