[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF FLORIDA]

Physical and Thermodynamic Properties of Terpenes. IV. The Dielectric Constant, Refractive Index and Density of Some Terpenes[1]

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RECEIVED MAY 7, 1954

The terpenes studied were α-pinene, β-pinene, terpinolene, α-terpinene, γ-terpinene, *d*-limonene, *l*-limonene, myrcene and alloöcimene, dipentene, pinane and Δ^3-carene. Densities, dielectric constants and refractive indexes at 25° were measured. A thoroughly tested heterodyne beat frequency apparatus was used for the determination of the dielectric constants.

Numerous values of the densities and refractive indexes of many terpene hydrocarbons have been reported in the literature. In many cases these values show a wide variation. Such variation is not surprising when it is realized that the samples used were frequently of questionable purity. No values for the dielectric constants of these hydrocarbons have been reported previously. For these reasons the present study was undertaken.

Experimental

Benzene.—This reagent was carefully purified by repeated fractional distillation and fractional crystallization. It was stored in brown bottles over sodium. The density and refractive index were found to be in close agreement with the values listed in the literature.[2] These are included in Table I.

TABLE I

DATA ON PHYSICAL PROPERTIES OF THE COMPOUNDS STUDIED

Compound	Density at 25°	n^{25}D	Dielectric constant (e)	MR_{D}
Benzene	0.8736	1.4982	2.273	...
Carbon tetrachloride	....	1.4574	2.227	...
α-Pinene	.8544	1.4631	2.1787	43.92
β-Pinene	.8673	1.4768	2.4970	44.36
d-Limonene	.8383	1.4701	2.3746	45.34
l-Limonene	.8384	1.4701	2.3738	45.38
Dipentene	.8370	1.4701	2.3810	45.42
Terpinolene	.8562	1.4860	2.2918	47.68
α-Terpinene	.8304	1.4760	2.4526	46.27
γ-Terpinene	.8458	1.4712	2.2738	45.03
Pinane	.8542	1.4603	2.1456	43.71
Δ^3-Carene	.8511	1.4698	2.1988	44.64
Myrcene	.7888	1.4680	2.3000	48.01
Alloöcimene	.8059	1.5420	2.5574	53.21

Carbon Tetrachloride.—The purest commercial carbon tetrachloride was subjected to a series of fractional distillations, washing with sulfuric acid, sodium hydroxide and water, drying over anhydrous sodium carbonate and refractionation. It was stored in brown bottles over stick potash. The refractive index and dielectric constants were found to agree very well with the values in the literature.[2] These values are listed in Table I.

α-Pinene.—α-Pinene was obtained as a commercial product of approximately 95% purity through the courtesy of The Glidden Company, Jacksonville, Florida. It was purified in five-liter batches by fractional distillation through a column of the Lecky and Ewell type.[3] The α-pinene had a constant boiling point of 52° (20 mm.); n^{25}D 1.4631. The product was stored under nitrogen until used.

β-Pinene.—β-pinene was obtained as a commercial product of approximately 95% purity through the courtesy of The Glidden Company, Jacksonville, Florida. It was purified in five-liter batches by fractional distillation through the column described in the above paragraph. The β-pinene was stored under nitrogen at −20°. Its refractive index at 25° was 1.4768, and its observed rotation in a one-decimeter tube was −18.20° at 25°.

α-Terpinene, γ-Terpinene and Terpinolene.—These terpenes were furnished through the courtesy of The Glidden Company, Jacksonville, Florida. They were obtained as by-products of the commercial process for making camphene by the isomerization of α- or β-pinene. Repeated fractionations of the by-product mixture accomplished the separation. The purities were stated as being greater than 98%. Each was washed with 15% sodium hydroxide solution to remove the inhibitor (ditertiary butyl *p*-cresol). After the terpenes had been dried with magnesium perchlorate they were carefully fractionated through a four-foot column packed with stainless steel wool at a reflux ratio of about 60 to 1. The constant-boiling fractions were checked frequently by refractive indexes. The fractions of each terpene with constant refractive index were combined. These samples were stored under nitrogen at −20°. The n^{25}D values for the purified compounds were: α-terpinene, 1.4760; γ-terpinene, 1.4712; terpinolene, 1.4860.

Pinane and Δ^3-Carene.—Samples of these compounds were furnished through the courtesy of the Naval Stores Experiment Station, United States Department of Agriculture, Olustee, Florida; no purification of them was attempted. Constants taken on the samples as received were: pinane, n^{25}D 1.4603, $[\alpha]^{25}$D −20.2°; Δ^3-carene, n^{25}D 1.4698.

***d*-Limonene.**—"Stripper Oil," an extract from orange peel containing a high percentage of *d*-limonene, was furnished through the courtesy of the Minute Maid Corporation, Plymouth, Florida. This oil was carefully fractionated, and the constant-boiling fraction (b.p. 71° (20 mm.), n^{25}D 1.4701) was collected. The specific rotation at 25° was +102.66°. The *d*-limonene was stored under nitrogen at −20°.

***l*-Limonene.**—A sample of *l*-limonene, prepared by the pyrolysis of β-pinene, was supplied by the Naval Stores Experiment Station, United States Department of Agriculture, Olustee, Florida. The specific rotation and refractive index of the samples at 25° were −90.3° and 1.4703, respectively. Careful fractionation of the 200-ml. sample through a four-foot column packed with stainless steel wool at reflux ratios greater than 60 to 1 produced 70 ml. of constant-boiling material with n^{25}D of 1.4701. The product was stored under nitrogen at −20°.

Dipentene and Alloöcimene.—Dipentene and alloöcimene were obtained as two of the products from the vapor phase pyrolysis of α-pinene.[4] They were supplied by the Naval Stores Laboratory, University of Florida. Separation of the components of the pyrolysis mixture was carried out by fractional distillation. The fraction boiling at 70–72° (20 mm.) was carefully refractionated through the column described under α-pinene. The dipentene boiled at 71° (20 mm.) and had a refractive index at 25° of 1.4701. It was collected and stored under nitrogen at room temperature.

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(1) This paper is abstracted from a portion of a dissertation submitted by Gerald A. Thomas to the Graduate Council of the University of Florida in partial fulfillment of the requirements for the degree of Doctor of Philosophy, August, 1952, and was presented at the Southwestern-Southeastern Regional Meeting, New Orleans, Louisiana, December 11, 1953.

(2) J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., Inc., New York, N. Y., 1950.

(3) W. D. Stallcup, R. E. Fuguitt and J. E. Hawkins, *Ind. Eng. Chem., Anal. Ed.*, **14**, 503 (1942).

(4) L. A. Goldblatt and S. Palkin, THIS JOURNAL, **63**, 3517 (1941).

The higher boiling fraction from the first distillation, consisting largely of alloöcimene, was carefully refractionated; that portion which had a boiling point of 90° (20 mm.) and a refractive index of 1.5420 at 25° was collected.

Myrcene.—A liter of 71 to 73% myrcene was furnished through the courtesy of The Glidden Company, Jacksonville, Florida. Careful fractionation of 500 ml. of this material produced 100 ml. of myrcene with a refractive index of 1.4680 at 25°. Since this material was stored for several weeks under nitrogen at room temperature, it was again fractionated before use in making capacity measurements. This second fractionation was carried out at 5 mm. pressure with special care being taken to avoid contact of the material with air. This was accomplished by use of a nitrogen atmosphere throughout the system. The myrcene was used for making solutions within a few minutes after being distilled. It was transferred to the weighing bottle in an atmosphere of nitrogen. The refractionated myrcene had a refractive index at 25° of 1.4680.

Apparatus.—The heterodyne beat apparatus was designed and built on the basic principles described by Stranathan[5] and Smyth.[6]

Improved and more readily available vacuum tubes were substituted for older tubes specified in the original circuits. Increased precision and ease of operation were realized by use of a 1000-cycle tuning-fork oscillator and subsequent tuning at each measurement to a point of no-beat in the 1000-cycle tone produced. A combination of the 1000-cycle fork with a cathode-ray oscilloscope increased the ease with which the tuning could be accomplished. A more complete description of the general principles of operation of such an apparatus is found in Weissberger's "Physical Methods of Organic Chemistry," Part II.[7]

The entire apparatus, including the precision condenser but exclusive of the test cell and its constant temperature bath, was housed in a standard 21.5″ × 15″ × 11″ metal cabinet.

The precision condenser was a General Radio Company Type 722D with high (100 to 1100 mmf.) and low (25 to 110 mmf.) scales. The instrument was furnished with a worm-correction calibration, making an accuracy of ±0.1 mmf. possible in the high scale range which was used in these measurements. Two terminals at the right side of the cabinet served for connection to the test cell which was immersed in a constant temperature bath. The ground lead was of heavy, insulated copper wire and was rigidly mounted in the same position for each measurement. The make-break connection to the test cell was made by means of a thumb-screw adjustment of an arc of piano wire dipping into a small pool of mercury on the lead of the test cell. This contact arrangement was in strict adherence to the recommendations for such connections and completely described by the manufacturer of the precision condenser.[8] Such an arrangement using the separation distance of one-quarter inch, as recommended, has been shown as the ideal method for eliminating a common source of error in capacity measurements.

The test cell, or condenser in which solutions are placed for capacity measurements, was a commercial model made by J. C. Balsbaugh of Cambridge, Massachusetts. The volume of liquid used in each test was 50 ml. The capacity of the cell was approximately 50 mmf. Special connectors were machined to make easy the connection of the cell terminals to the ground lead and arc make-break contact already described. The cell was readily removable from the bath for cleaning and filling. The bath liquid was mineral oil. The temperature of the mineral oil was held at 25 ± 0.02°. The thermoregulator was set and checked at 25° by use of a Bureau of Standards calibrated platinum resistance thermometer.

The procedure in normal operation of the apparatus included tuning the precision condenser, making and breaking contact with the test cell, and turning the audio-oscillator and the oscilloscope on and off.

Several weeks of testing the apparatus established (1) the necessity of a Sola H-51 constant voltage transformer on the 115-volt line voltage, (2) the stabilizing influence of housing the apparatus in a constant-temperature (±1°) room, and (3) the need for a standardized procedure and position for the operator.

Refractive indexes of the terpenes used were measured with an Abbe refractometer calibrated with liquids certified by the U. S. Bureau of Standards.

Densities of the volatile terpenes were determined with pycnometers of the Lipkin type,[9,10] which are commercially available.[11]

The pycnometers were calibrated with freshly distilled water. All volume readings were taken while the pycnometers were immersed in a water-bath held at 25° (±0.03°). A magnifying glass was used to make more accurate readings of the liquid levels in the capillary side-arms of the pycnometers. At least 30 minutes were allowed for the pycnometers and contents to come to the temperature of the bath. After careful wiping with a moist chamois skin the pycnometers were put into the outer balance case for 30 minutes and then weighed.

Weighings were made on a Christian Becker Semimicro balance readable directly to the fifth decimal place. To eliminate corrections for the volume occupied by glass, a tare pycnometer was used in the density determinations. All weights were reduced "to vacuum."

The transfer of the terpenes from one container to another was always made in an atmosphere of nitrogen. A hand-pressed rubber bulb was used for filling the larger pipets. Nitrogen was blown into the space above the liquid in the weighing bottle after the introduction into the bottle and before weighing.

Procedure.—The apparatus was allowed to warm up for more than six hours. The test cell was washed successively with alcohol, acetone and alcohol. The outer member of the test cell was dried with a stream of dry nitrogen while the inner member was allowed to drain free of alcohol. The cell was then put into the constant temperature bath. A stream of dry nitrogen was introduced at the bottom of the cell by means of a 3 mm. o.d. Pyrex glass tube which could be passed between the members of the ground glass joint when the central, or inner, portion was raised about one inch. The nitrogen removed all traces of alcohol and filled the cell with nitrogen. A sensitive test of dryness was the measuring of the capacity of the cell.

The capacity of the cell was recorded as the average of four to six settings of the instrument with the cell in and with the cell out of the circuit. These settings were taken over a period of one-half hour. The capacity of the "empty" (nitrogen-filled) cell was taken before every measurement was made on a compound or solution. A 50-ml. pipet was used to transfer benzene into the test cell. Thirty minutes were allowed for the benzene to come to the temperature of the bath. The capacity of the cell containing benzene was recorded as the average of four to six settings over at least one-half hour with the cell in and with the cell out of the circuit.

Each compound was handled in the same way as described above for benzene and then placed in tightly closed containers to be used later for determination of densities.

Calculations

Molar Refraction.—The refractive indexes of the compounds used were measured with an Abbe refractometer and were calculated according to the equation

$$MR_D = \frac{n^2 - 1}{n^2 + 2} \times \frac{M}{d}$$

where MR_D is the molar refraction, n is the refractive index, M is the molecular weight and d is the density.

Standardization of the dielectric constant measuring cell using pure benzene (dielectric constant

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(5) J. Stranathan, *Rev. Sci. Instruments*, **5**, 334 (1934).

(6) C. P. Smyth, "Dielectric Constant and Molecular Structure," Chapter III, Chemical Catalog Co., New York, N. Y., 1931.

(7) A. Weissberger, "Technique of Organic Chemistry, Physical Methods of Organic Chemistry," Vol. I, Part II, Chapter XXIV, C. P. Smyth, Interscience Publishers, Inc., New York, N. Y., 1949.

(8) "The General Radio Experimenter," Vol. XXI, No. 12, May, 1947; Vol. XXI, No. 1, June, 1947.

(9) M. R. Lipkin, J. A. Davison, W. T. Harvey and S. S. Kurtz, Jr., *Ind. Eng. Chem.*, *Anal. Ed.*, **16**, 55 (1944).

(10) A. S. T. M. Standards, 1945 Suppl., Part III, p. 164.

(11) Ace Glass Co., Vineland, N. J.

2.273 at 25°)[2] was carried out in the usual way. The standardization was checked using pure carbon tetrachloride (2.227 at 25°).[2]

Instead of using values for C_0 and C_L in each dielectric constant calculation, the following formula was derived for use in making the calculation directly from measurement recordings

$$e = 1 + (1.273)\frac{C' - C}{C' - C}$$

where C is the capacity with nitrogen in the cell, C' is the capacity with the liquid in the cell, and C'' is the capacity with benzene in the cell.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF NEW BRUNSWICK]

The Determination of the Rate Constants for the Recombination of Phenylglyoxylate Anions with Various Proton Donors

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RECEIVED APRIL 19, 1954

The recombination of phenylglyoxylate ions with protons was studied by measuring rate-controlled polarographic currents of the undissociated acid in the pH range in which the kinetic current is about 200 times smaller than the total diffusion current. The experimental data were found in full agreement with the theory based on participation of hydronium ions, water and boric acid as proton donors and the equations for fully rate-controlled currents developed earlier. The following values for individual rate constants of recombination were determined at 25°: $k_{H_3O^+} = 5.73 \times 10^{10}$ l. moles^{-1} sec.$^{-1}$ $k_{H_2O} \times [H_2O] = 22$ sec.$^{-1}$, $k_{H_3BO_3} = 6.38 \times 10^2$ l. moles^{-1} sec.$^{-1}$. While the accuracy of the values determined for $k_{H_3O^+}$ is approximately ±10%, the values for k_{H_2O} and $k_{H_3BO_3}$ are accurate only to ±30% and thus indicate only the order of magnitude of these constants.

Introduction

It was shown in the year 1946[2] that with acids, which gave rise in buffer solutions to separate polarographic waves of the undissociated acid and the acid anion, the pH at which the more positive wave of the undissociated acid becomes equal in height to the more negative wave of the anion may be shifted to higher values with respect to the pH of half-neutralization of the particular acid. This shift is a function of the recombination velocity of the particular acid anion with protons. In most cases the wave of undissociated acid is still obtained in solutions of such a pH that the undissociated acid can be present only in negligible concentration; in such instances the whole current due to the undissociated acid is kinetic in character.

If the concentrations of all the components of the system are constant,[3] an expression for the velocity constant may be obtained by substituting $\mu = {}^1/_2\sqrt{2D/k'}$ in the equation of Brdička and Wiesner[2] (μ = effective thickness of the interface, D = diffusion constant, k' = pseudo-unimolecular rate constant of the dissociation reaction). In a more complete mathematical analysis of the problem Koutecký and Brdička[4] have shown that for regions where the current of the undissociated acid is negligibly small the above expression is justified. The expression for μ as derived in this paper was $\mu = \sqrt{D/k'}$, and differs therefore only by the factor $\sqrt{2}$ from the one mentioned above.

The general equations of Koutecký and Brdička make it possible to calculate the ratio of the acid and anion wave for every pH including those where the acid wave is approaching in height the sum of both. For phenylglyoxylic and pyruvic acids the expected dependence of this ratio on the pH, calculated on the assumption that the only important mechanism of proton transfer is the reaction with hydronium ions, was given in the paper of Koutecký and Brdička.[4] It was found to deviate slightly but reproducibly from the experimental results.

Proton transfer in a buffered solution containing a reducible acid AH and a buffer acid BH may be expected to proceed through the following reactions

$$A' + H_3O^+ \underset{k_1'}{\overset{k_1}{\rightleftarrows}} AH + H_2O \qquad (\mathrm{I})$$

$$A' + H_2O \underset{k_2'}{\overset{k_2}{\rightleftarrows}} AH + OH' \qquad (\mathrm{II})$$

$$A' + BH \underset{k_3'}{\overset{k_3}{\rightleftarrows}} AH + B' \qquad (\mathrm{III})$$

Hanuš[5] has studied in detail the effect of buffer on the ratio of the acid and anion wave of phenylglyoxylic acid in the pH region in which both are of the same order of magnitude. He found that in this region the reaction III is negligible. He arbitrarily neglected reaction II and in effect assumed that proton transfer takes place by reaction I. Ruetschi and Trümpler[6] also neglected the action of proton donors other than hydronium ions. However the reason which these authors give for neglecting reaction II, namely, the approach of the kinetic current to zero in sufficiently alkaline solutions, is not correct.

Experimental Part

It is shown in this communication that phenylglyoxylic acid (AH) gives, in borate buffer (at 25°)

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(1) This paper is abstracted from a part of the thesis to be submitted by Mary Wheatley in partial fulfillment of the degree of Doctor of Philosophy.

(2) R. Brdička and K. Wiesner, *Chem. Listy*, **40**, 66 (1946).

(3) K. Wiesner, *ibid.*, **41**, 6 (1947).

(4) J. Koutecký and R. Brdička, *Collection Czech. Chem. Communs.*, **12**, 337 (1947).

(5) V. Hanuš, "Proceedings of the First Polarographic Congress in Prague 1951," Part I, Published by Přírodovědecké Vydavatelství, Prague, p. 811.

(6) P. Ruetschi and G. Trümpler, *Helv. Chim. Acta*, **35**, 1957 (1952).