[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Microwave Absorption and Molecular Structure in Liquids. IV. The Dielectric Losses and Absolute Dielectric Constants of Some Non-polar Liquids[1]

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In the course of investigations of the microwave absorption of polar substances in solution in non-polar liquids, it was necessary to make careful measurements of the dielectric constants of the non-polar liquids. As these measurements are absolute determinations in contrast to the usual relative measurements carried out at radio frequencies and based upon the value of some liquid, usually benzene, taken as standard, it seems desirable to make the values generally available, although extreme precision cannot be claimed for them. The values also lead to conclusions of some theoretical interest.

Purification of Materials

n-Heptane from the Paragon Testing Laboratories was distilled in a four-foot packed column and the middle fraction drawn off. This fraction was then dried over sodium wire from which it was subsequently distilled. The middle fraction was used; b. p., 97.60–97.68° at 753 mm., $n^{20}\text{D}$ 1.38824; lit.,[2] b. p. 98.4°, $n^{20}\text{D}$ 1.38774.

C. P. benzene from the City Chemical Corporation, New York, was twice fractionally crystallized and dried over sodium wire. It was distilled in a four-foot column and the middle fraction collected; b. p., 79.80–79.85° at 760.9 mm.; $n^{20}\text{D}$ 1.50092; lit.,[3] b. p. 80.07°, $n^{20}\text{D}$ 1.50096.

Cyclohexane from the Paragon Testing Laboratories was distilled in a four-foot column and the middle fraction dried over sodium wire. This fraction was distilled after drying and the middle fraction drawn off; b. p., 80.30–80.40° at 760 mm., $n^{20}\text{D}$ 1.42656; lit.,[4] b. p., 80.7° at 760 mm., $n^{20}\text{D}$ 1.42648.

Carbon tetrachloride[5] from the Geo. A. Rowley Co., Philadelphia, was shaken with concentrated sulfuric acid, washed with separate portions of dilute sodium carbonate solution, then washed with distilled water until free from alkali, and dried over calcium chloride. The sample was distilled in a four-foot packed column and the middle fraction collected; b. p. 76.60–76.70°, m. p., −22.8°, $n^{20}\text{D}$ 1.46075; lit.,[6] b. p. 76.66°, m. p. −22.81°, $n^{20}\text{D}$ 1.46048.

Carbon disulfide was shaken with aqueous potassium permanganate solution (5 g./liter) and permitted to stand for thirty minutes. After separation with a separatory funnel the sample was shaken with mercury and then with successive portions of aqueous mercuric sulfate until free from the characteristic rancid odor. The sample was dried over calcium chloride and distilled through a four-foot packed column; b. p., 46.15–46.18° at 762.6 mm.; lit.,[7] b. p. 46.25° at 760 mm.

Experimental Method and Results

The absolute dielectric constants of the five non-polar liquids investigated in this research were determined at microwave frequencies by the methods described in an earlier publication.[8] All of the microwave dielectric constant values depend upon the accurate measurement of the wave length in the dielectric-filled section of the waveguide or coaxial cell. The 3.22 cm. values for *n*-heptane and benzene were carried out by Mr. A. D. Franklin using waveguide techniques. The 10 cm. values were determined with the use of a coaxial cell whereas the 577 m. values, which are relative values based upon the value of benzene at 25°, were measured with a heterodyne-beat apparatus previously described.[9] The 1.277 cm. values, like the 3.22 cm. values, were determined by waveguide methods. The microwave absorption technique used to obtain the dielectric losses of benzene, cyclohexane and *n*-heptane at 1.277 cm. listed in Table III for 20° will be described in detail in a later paper of this series.

The absolute dielectric constant values listed in Table I have been taken from dielectric constant *vs.* temperature plots. For the 1.277 cm. and 3.22 cm. determinations, equation (1) was employed to calculate the dielectric constants

$$\epsilon' = (\lambda_0/\lambda_d)^2 + (\lambda_0/\lambda_c)^2 \qquad (1)$$

The dielectric constants obtained with the coaxial transmission line cell were calculated from equation (2), since for a coaxial transmission line λ_c, the cutoff wave length, is infinite.

$$\epsilon' = (\lambda_0/\lambda_d)^2 \qquad (2)$$

In equations (1) and (2), λ_0 represents the free-space wave length, λ_d, the wave length in the dielectric medium, and λ_d, the cutoff wave length of the waveguide. The 577 m. radio frequency values have been calculated in the usual manner from the ratios of the dielectric-filled to the air-filled condenser capacitances. From the 10-cm. determination for benzene the value of 2.276 at 25° was chosen to calibrate the cell used in the heterodyne-beat apparatus. This value is identical with that used for many years for calibration of the radio frequency cells in this Laboratory. The probable error in the measurements at 577 m. is approximately ±0.2%, while for the microwave measurements, it is ±0.1%. Since the experimental values show no departure from a linear dependence upon temperature within the ranges of temperature covered by the measurements, they may be represented by an equation,

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(1) This research was carried out with the support of the Office of Naval Research.

(2) Egloff, "Physical Constants of Hydrocarbons," Vol. I, Reinhold Publishing Corp., New York, N. Y., 1939, p. 40.

(3) Egloff, "Physical Constants of Hydrocarbons," Vol. III, Reinhold Publishing Corp., New York, N. Y., 1946, p. 25.

(4) Egloff, "Physical Constants of Hydrocarbons," Vol. II, Reinhold Publishing Corp., New York, N. Y., 1940, p. 78.

(5) Purified by Mr. R. W. Crowe.

(6) Huntress, "Organic Chlorine Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 571.

(7) Timmermanns and Martin, *J. chim. phys.*, **25**, 411 (1928).

(8) Heston, Hennelly and Smyth, THIS JOURNAL, **70**, 4093 (1948).

(9) Lewis and Smyth, *J. Chem. Phys.*, **7**, 1085 (1939).

$\epsilon_t = a - bt$ for the temperature ranges indicated in Table II, where a is the measured or extrapolated dielectric constant at 0°, $-b$ is the slope of the line, and t is the centigrade temperature. Although the dielectric constant values at each wave length were treated separately to obtain the interpolated values given in Table I, the values were found to be independent of the wave length within the experimental error of the measurements. Consequently, a single equation is used to represent all the values for each substance. The values of the constants a and b and the temperature ranges of the individual measurements are given in Table II.

TABLE I

ABSOLUTE DIELECTRIC CONSTANT VALUES

	Temp., °C.	577 m.	10.00 cm.	3.22 cm.	1.277 cm.
n-Heptane	0	1.953	1.948	1.948	1.949
	20	1.924	1.920	1.920	1.920
	40	1.895	1.891	1.892	1.891
	60	1.866	1.863	1.864	1.862
Benzene	10	...	2.305	2.305	2.304
	20	...	2.286	2.285	2.284
	40	...	2.246	2.245	2.243
	60	...	2.206	2.205	2.203
Cyclohexane	10	2.040	2.041		2.039
	20	2.023	2.024		2.023
	40	1.989	1.992		1.990
	60	1.956	1.959		1.957
Carbon tetrachloride	0	2.276	2.278		2.278
	20	2.239	2.240		2.240
	40	2.203	2.204		2.203
	60	2.167	2.166		2.165
Carbon disulfide	0	2.691	2.692		2.695
	10	2.666	2.667		2.669
	20	2.641	2.642		2.643
	30	2.615	2.617		2.617

TABLE II

DIELECTRIC CONSTANTS AND THEIR TEMPERATURE DEPENDENCE

	a	b	Range, °C.
n-Heptane	1.948	0.00160	0–60
Benzene	2.325	.00200	10–60
Cyclohexane	2.056	.00163	10–60
Carbon tetrachloride	2.278	.00187	0–60
Carbon disulfide	2.692	.00252	0–30

The dielectric loss values given in Table III were measured using a double minimum standing wave ratio (SWR) method to be described fully later.

TABLE III

DIELECTRIC LOSS AND LOSS TANGENT AT 20° FOR 1.277 CM.

	ϵ''	tan δ
n-Heptane	0.00060	0.00031
Benzene	.0011	.00048
Cyclohexane	.00072	.00036

Discussion of Results

The 577 m. values for ϵ' obtained by the heterodyne beat method, the 10.00 cm. values obtained with a coaxial cell, and the 3.22 cm. and 1.277 cm. values obtained by waveguide techniques differ from one another by less than the probable absolute errors in the measurements. As the measurements at the three different centimeter wave lengths are absolute determinations, they give absolute dielectric constant values, which confirm, within their limits of accuracy, the correctness of the value previously used for benzene as a standard liquid.

If these presumably non-polar molecules had considerable dipole moments, the dielectric constants would vary strongly with frequency in the microwave region and the liquids would exhibit considerable dielectric loss,[8,10,11] which would affect the dielectric constant as shown by equation (3)

$$\epsilon' = (\lambda_0/\lambda_d)^2 + (\lambda_0/\lambda_c)^2 - (\epsilon''\lambda_d/2\lambda_0)^2 \qquad (3)$$

However, the ϵ'' values in Table III are so small that their insertion in equation (3) shows their effect upon the dielectric constant values to be undetectable. The loss values are of the same order of magnitude as those observed by Whiffen[12] and Bleaney, Loubser and Penrose.[12] Whiffen measured a number of non-polar liquids from 3.5 to 0.8 cm. by a cavity resonator method, which was more accurate for loss measurements than the method used in the present work, and attributed the losses to the presence of small moments produced by the bending or stretching of bonds. The possibility that these small losses may be due to traces of impurities, notably water, is reduced by the precautions observed by Whiffen and the adequacy of the agreement between his results and the approximate values in Table III.

With the exception of carbon tetrachloride, these molecules are anisotropic, which would result in a tendency for the molecules to orient with their axes of maximum polarizability in the direction of the electric field of the microwave. The extent of this orientation is so small that the effect of its lag behind the high frequency field of the microwave is too small to detect in these dielectric constant measurements and would be observable only by a method possessing the precision of the optical method used in Kerr effect measurements.

Although dipole moment determinations by means of dielectric constant measurements show moment values experimentally indistinguishable from zero, even measurements on the molecules in the vapor state hardly distinguish between zero and 0.1 D for the moment. The microwave absorption method used to measure the dielectric losses given in Table III is no more reliable than

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(10) Laquer and Smyth, THIS JOURNAL, **70**, 4097 (1948).

(11) Hennelly, Heston and Smyth, *ibid.*, **70**, 4102 (1948).

(12) Whiffen, in press; Bleaney, Loubser and Penrose, *Proc. Phys. Soc. (London)*, **59**, 185 (1947).

±25% for such low dielectric loss. If the value of the dielectric loss for each of the three substances measured is substituted in the Debye equation as used by Jackson and Powles[13] and given in equation (4), a moment value 0.04 D is calculated for benzene, n-heptane and cyclohexane.

$$\mu = \left[\frac{27\,\epsilon''\,kT\,(1 + (2\pi f\tau)^2)}{8(\epsilon' + 2)^2 N c \pi^2 f\tau}\right]^{1/2} \tag{4}$$

where μ is the dipole moment, ϵ'' is the dielectric loss, ϵ' is the dielectric constant, T is the absolute temperature, k is the Boltzmann constant, f is the frequency in cycles per second, τ is the relaxation time in seconds, N is Avogadro's number, and c is the density divided by the molecular weight. In the calculation of the dipole moment by this method the value of τ, the relaxation time, has been assumed to be approximately 5×10^{-12} seconds in view of the values of τ found for bromobenzene, cyclohexyl bromide and n-heptyl bromide at 25° in the 1.27 cm. measurements.[11] These moment calculations seem to indicate that moment values between 0 and 0.1×10^{-18} may be differentiated by the use of microwave absorption methods. However, these small moment values indicated by the losses are not to be interpreted as evidencing permanent asymmetry of the molecules.

Summary

The dielectric constants of n-heptane, benzene, cyclohexane, carbon tetrachloride and carbon disulfide have been measured at 577 m., 10 cm. and 1.277 cm., while additional values at 3.22 cm. have been obtained for n-heptane and benzene. The measurements at 10 cm., 3.22 cm. and 1.277 cm. are absolute determinations. The values are independent of frequency since the losses measured at 1.277 cm. for three of the non-polar liquids are so low as to be negligible in their effect on the dielectric constant. The absolute dielectric constant values are linear functions of the temperature within the accuracy of the measurements.

The dielectric loss values at 1.277 cm. have been used to calculate extremely low moment values for n-heptane, benzene and cyclohexane, possibly, the result of inductive effects. The calculations indicate that microwave absorption results may be used to differentiate between moment values of 0 and 0.1×10^{-18}.

PRINCETON, NEW JERSEY RECEIVED JUNE 23, 1949

[13] Jackson and Powles, *Trans. Faraday Soc.*, **42A**, 101 (1946).

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

Photochemical Studies. XLII. Ethylene Oxide[1]

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The only previous work on the photochemistry of ethylene oxide seems to be that of Phibbs, Darwent and Steacie[3] who investigated its mercury sensitized reactions. Trost, Darwent and Steacie[4] have studied the reactions of hydrogen atoms with ethylene oxide. The thermal reactions of this molecule have been studied extensively.[5]

The ultraviolet absorption spectrum of ethylene oxide has been photographed and interpreted recently.[6] The longest wave discontinuous absorption is found at 1713 Å. This band broadens as the pressure is increased and gives an apparent continuum to about 2120 Å.

The first experiments (carried out with a hydrogen discharge as a light source) served to show that the principal products of the direct photochemical decomposition of ethylene oxide are hydrogen, carbon monoxide, methane and ethane. Since hydrogen gas probably could not be formed unless H atoms are produced in the primary process, the work of Phibbs, Darwent and Steacie is of importance in interpreting the results of the present research. The production of methane and of ethane indicates, presumably, that CH_3 radicals are intermediates. The reactions of CH_3 radicals (formed by photochemical decomposition of mercury dimethyl) with ethylene oxide were also studied. A recent investigation[7] has served to clarify certain steps in the photochemical decomposition of mercury dimethyl.

Experimental

The ethylene oxide was specially purified by the Dow Chemical Company.[8] It was purified further by bulb-to-bulb distillation and outgassed in a high vacuum after cooling to −120°. It was free from aldehydes as shown by the method of Stotz.[9]

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* Harvard University Postdoctoral Fellow 1949–.

(1) This work was supported in part by Contract N6onr-241, Task I, with the Office of Naval Research, United States Navy.

(2) E. I. du Pont de Nemours and Company Fellow, 1948–1949.

(3) M. K. Phibbs, B. de B. Darwent and E. W. R. Steacie, *J. Chem. Phys.*, **16**, 39 (1948).

(4) W. R. Trost, B. de B. Darwent and E. W. R. Steacie, *ibid.*, **16**, 357 (1948).

(5) For a summary see E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corporation, New York, N. Y., 1946, pp. 139, 308, 368 and 395.

(6) Ta-kong Liu and A. B. F. Duncan, *J. Chem. Phys.*, **17**, 241 (1949).

(7) R. Gomer and W. A. Noyes, THIS JOURNAL, **71**, 3390 (1949).

(8) The authors wish to express their appreciation to Dr. D. R. Stull of the Dow Chemical Company who prepared the ethylene oxide for Dr. W. D. Walters of this Department.

(9) E. H. Stotz, *J. Biol. Chem.*, **148**, 585 (1943). This method has been the subject of further study by W. F. Erbelding and W. D. Walters of this Laboratory.