in carbon disulfide, filtered and n.m.r. spectra recorded. Preparation of the sample for analysis was accomplished by removing the carbon disulfide under vacuum and resubliming the isolated decaborane into an appropriate receiver. Larger scale reactions, employing 0.05 mole of decaborane, were carried out with the same procedure. Elemental analysis of the final exchange product revealed only a trace amount of chlorine and less than 1% carbon.

The dioxane exchanges of tetradeuteriodecaborane with deuterium and hydrogen chloride were carried out in the same manner as described above using approximately the same molar ratios of reactants.

Deuterium Analyses.—The percentage of deuterium in any given decaborane sample was determined using the pyrolysis method previously described.[6,18] The mass spectrometer (Consolidated Engineering Corporation, type 21–620) was calibrated using equilibrium mixtures of H_2, HD and D_2 prepared by the decomposition of known mixtures of water and deuterium oxide on zinc at 400°.[19] The precision of the above method was approximately 1% and the accuracy was estimated to be within 2%.

N.m.r. Spectra.—The B^{11} and H^1 n.m.r. spectra were obtained with a Varian High Resolution Spectrometer operating at 12.8 and 40 mc., respectively. All B^{11} n.m.r. spectra in any given series were recorded at essentially the same sweep rate and chart speed.

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change samples produces no detectable amount of internal H-D exchange. This is readily apparent from the fact that exclusively bridge deuteronated decaborane is obtained by sublimation of a 45 hr.-DCl/dioxane exchange sample. Furthermore, no detectable change in either the H^1 or B^{11} n.m.r. spectra is observed after sublimation of the various electrophilic exchange-samples.

(18) J. Graff and David Rittenberg, *Anal. Chem.*, **24**, 878–881 (1952).

(19) "Physical Properties and Analysis of Heavy Water," Isidor Kirshenbaum, McGraw-Hill Book Co., Inc., New York, N. Y., 197–201 (1951).

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY, PRINCETON, N. J.]

The Dielectric Relaxation of Dibromodichloromethane, Succinonitrile and Several Camphor Derivatives in the Solid State[1,2]

BY DONALD E. WILLIAMS AND CHARLES P. SMYTH

RECEIVED OCTOBER 28, 1961

The dielectric constant and loss at 3.2 cm. wave length have been measured over a wide range of temperature for *dl*-camphene, *d*-camphor, *dl*-camphor, *d*-camphoric anhydride, *dl*-isoborneol, dibromodichloromethane and succinonitrile in the solid state. All of them show molecular orientational freedom in the crystal lattice over a considerable range of temperature. Dielectric relaxation times have been obtained for all of the solids and heats and entropies of activation have been calculated for five of them. The rotational freedom of these molecules in the crystal lattice between the freezing point and a transition point is comparable to that in the liquid state.

Very extensive dielectric investigations have been carried out on the rotational or orientational freedom of molecules in the solid state.[3] Most of the molecules investigated have fallen into one of two categories. Either they have been fixed so rigidly in the crystal lattice that they could not orient at all in the electric field used in the measurements, or they have possessed sufficient rotational freedom to orient in radio frequency fields without appreciable relaxation effects. Measurements of dielectric constant and loss at 3.22 cm. wave length carried out in this Laboratory upon *d*-camphor[4] and upon six tetrasubstituted methanes[5] gave information concerning the relaxation of the molecules in the crystal lattice. This paper reports similar measurements with some improvements in technique upon five bicyclic terpenes, dibromodichloromethane and succinonitrile, all save two of which had previously been measured at radio frequencies.[6–8]

Purification of Materials.—*dl*-Camphene, supplied by The Matheson Company, Inc., was twice recrystallized from ethyl alcohol and then repeatedly melted and frozen under a 3 cm. vacuum; m.p. 50°; literature[9] m.p. 51–52°, transition temperature −108°.

d-Camphor, supplied by Eastman Kodak Co., was twice recrystallized from ethyl alcohol and then sublimed; m.p. 176°; literature m.p. 177.6°,[6] 179.75°[9]; transition temperature 28°; literature,[6] 28°.

dl-Camphor (synthetic), supplied by The Matheson Company, Inc., was measured as received; m.p. 178.0°; literature[10] m.p. 178.8°; transition temperature −67°, literature[9] −66°.

d-Camphoric anhydride, supplied by The Matheson Company, Inc., was recrystallized from ethyl alcohol and vacuum dried for three days; m.p. 218°; literature 216–217°, 223.5°[11]; transition temperature 133°; literature[11] 135°.

dl-Isoborneol, supplied by The Matheson Company, Inc., was recrystallized twice from ethyl alcohol and then sublimed; m.p. (sealed tube) 212°; literature[12] m.p. (sealed tube) 212°; transition temperature 8–9°.

Dibromodichloromethane from The Matheson Company, Inc., was recrystallized from the melt four times and measured immediately, m.p. 22°; literature 22°.

Succinonitrile, supplied by Matheson, Coleman and Bell, Inc., was vacuum distilled. The middle fraction was taken; f.p. 57.2°; literature 57.15–57.20°.[13]

Methods of Measurement.—Dielectric constants and losses were measured at a wave length of 3.19 cm. by methods described in part in a previous paper[5] and in full in the thesis

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(1) This research was supported in part by the Office of Naval Research. Reproduction, translation, publication, use or disposal in whole or in part by or for the United States Government is permitted.

(2) This paper represents a part of the work submitted by Donald E. Williams to the Graduate School of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., New York, N. Y., 1955, Chap. V.

(4) J. G. Powles, *J. Chem. Phys.*, **20**, 1648 (1952).

(5) J. G. Powles, D. E. Williams and C. P. Smyth, *ibid.*, **21**, 136 (1953).

(6) W. A. Yager and S. O. Morgan, *J. Am. Chem. Soc.*, **57**, 2071 (1935).

(7) A. H. White and W. S. Bishop, *ibid.*, **62**, 8 (1940).

(8) A. H. White and S. O. Morgan, *J. Chem. Phys.*, **5**, 655 (1937).

(9) "The Merck Index," 6th Ed., Merck and Co., Inc., Rahway, N. J., 1952, p. 194.

(10) I. Heilbron and H. M. Bunbury, "Dictionary of Organic Compounds," Eyre and Spottiswoode, London, 1953.

(11) L. O. Fisher, *Bull. soc. chim. belges*, **49**, 129 (1940).

(12) Ref. 9, vol. III, p. 65.

(13) J. Timmermanns and Mme. Hennaut-Roland, *J. chim. phys.*, **34**, 693 (1937).

of one of the authors.[14] The solid sample for measurement was forced into a cell with pressures up to 40,000 pounds per sq. in. with a press made available to us by the Plastics Laboratory of the University. The cell consisted primarily of a brass block with a hole cut through it to fit the inside cross-section of the waveguide. The solid sample was pressed into this hole between stainless steel plates to form a uniform clear slab, the thickness of which was measured with a pair of micrometer calipers to 0.001 in. The back and front of the slab were then covered with mica windows, which were held in place, respectively, by a short-circuit plate and a cover plate. The dielectric constant and loss were measured in this short-circuited cell by a standing-wave method.[14]

The so-called static dielectric constant was measured for *dl*-camphene and *dl*-isoborneol with an impedance bridge[15] at a frequency of 5 kilocycles. The *dl*-camphene was melted into a concentric cylinder cell as in many previous measurements in this Laboratory. The high-melting *dl*-isoborneol was obtained as a pressed sample by the use of three telescoping brass tubes. The middle tube was used to press the solid between the other two tubes, which served as the measuring condenser.

The values of the static dielectric constant, ϵ_0, actually measured at 5 kc. or taken from the literature[6,7] with adjustment for density differences,[14] the dielectric constant at 3.19 cm. wave length, ϵ', and the dielectric loss at 3.19 cm., ϵ'', are plotted against temperature in Figs. 1–6. The dielectric loss has been plotted against dielectric constant for each substance to obtain Cole–Cole arc plots, from which the critical wave lengths, the corresponding relaxation times and the distribution parameters are obtained.[16] For *dl*-camphene, *d*-camphor, *dl*-camphor and *d*-camphoric anhydride, plots of the logarithm of the critical wave length against the reciprocal of the absolute temperature give excellent straight lines from which the heats $\Delta H^{\ddagger}$ and entropies $\Delta S^{\ddagger}$ of activation[15] are obtained.[5] These calculated values are given in Table I.

TABLE I

CRITICAL WAVE LENGTHS, RELAXATION TIMES, DISTRIBUTION PARAMETERS AND HEATS AND ENTROPIES OF ACTIVATION

dl-Camphene, $\Delta H^{\ddagger}$, 1.6 ± 0.1 kcal.; $\Delta S^{\ddagger}$, −5 ± 0.3 e.u.

Temp., °C.	−100	−60	−20	0	20
λ_m (cm.)	20.7	5.50	3.75	2.89	2.38
τ (10^{-12} sec.)	110	27.9	19.9	15.3	12.6
α	0.44	0.22	0.00	0.00	0.00

d-Camphor, $\Delta H^{\ddagger}$, 2.7 ± 0.2 kcal.; $\Delta S^{\ddagger}$, −1 ± 0.6 e.u.

Temp., °C.	−20	20	40	60	100	140
λ_m (cm.)	10.12	3.89	2.92	2.44	1.53	1.07
τ (10^{-12} sec.)	53.4	20.6	15.5	13.0	8.13	5.68
α	0.12	0.04	0.00	0.00	0.00	0.00

dl-Camphor, $\Delta H^{\ddagger}$, 2.6 ± 0.1 kcal.; $\Delta S^{\ddagger}$, 2 ± 0.3 e.u.

Temp., °C.	−60	−20	20	60	100	140
λ_m (cm.)	51.7	8.29	4.02	2.30	1.55	1.12
τ (10^{-12} sec.)	274	44.0	21.3	12.2	8.23	5.95
α	0.28	0.14	0.07	0.00	0.00	0.00

d-Camphoric anhydride, $\lambda_m \cong 0.6$ cm. at 140°; $\tau \cong 3.2 \times 10^{-12}$ sec. at 140°.

dl-Isoborneol, $\Delta H^{\ddagger}$, 4.0 ± 0.2 kcal.; $\Delta S^{\ddagger}$, 2 ± 0.6 e.u.

Temp., °C.	20	40	60	80	100	120
λ_m (cm.)	4.42	2.18	1.49	1.23	0.91	0.68
τ (10^{-12} sec.)	23.5	11.6	7.91	6.54	4.83	3.61
α	0.36	0.27	0.09	0.00	0.00	0.00

Dibromodichloroethane, $\lambda_m = 0.4 \pm 0.1$ cm. at 20°; $\tau = 2.1 \times 10^{12}$ sec.

Discussion of Results

The low polarity of the *dl*-camphene molecule results in low values for the dielectric constant and loss (Fig. 1). The significance of the apparent minimum in the static dielectric constant is not certain. The increase with rising temperature as the melting point is approached seems to parallel similar behavior for solid benzene observed in this Laboratory, which may have arisen from unfilled spaces between the electrodes. The decrease as the temperature rises above the transition point is the normal effect of temperature upon the orientation of polar molecules. With the disappearance of molecular orientation in the applied field below the transition point, the static dielectric constant seems to drop below the dielectric constant at 3.19 cm., but this apparent discrepancy is probably due to incomplete filling of the space between the condenser cylinders. The small loss at 3.19 cm. below the transition point indicates the persistence of a trace of the molecular orientational freedom evident above the transition and evident also in the further decrease of the static dielectric constant below the transition.

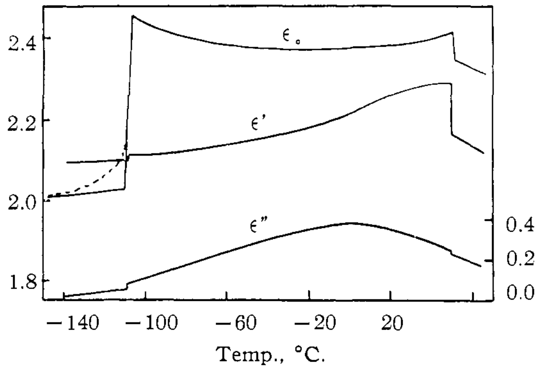

Fig. 1.—Static (5 kc.) dielectric constant, ϵ_0, and dielectric constant, ϵ', and loss, ϵ'', at 3.19 cm. wave length as a function of temperature for *dl*-camphene. The dashed line represents values uncorrected for the inhomogeneity of the sample.

Although *d*-camphor was measured[4] in this Laboratory a year or two before the present measurements were carried out, it is believed that the improved techniques used in the present measurements make them worth inclusion in this paper. The large dipole of *d*-camphor (Fig. 2) causes the dielectric constant and loss to be much larger than those of *d*-camphene. The low-frequency or static

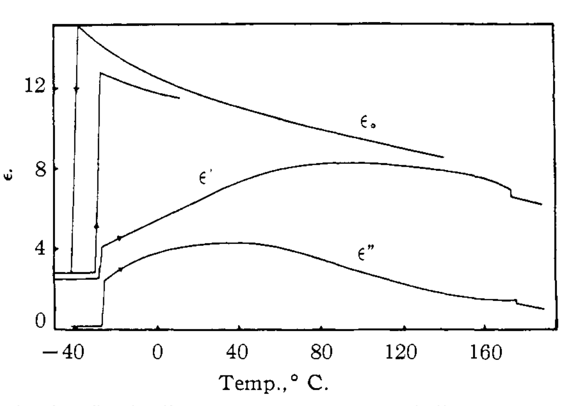

Fig. 2.—Static dielectric constant, ϵ_0, and dielectric constant, ϵ', and loss, ϵ'', at 3.19 cm. wave length as a function of temperature for *d*-camphor.

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(14) D. E. Williams, "Dielectric Relaxation in the Rotator State," Ph.D. Thesis, Princeton University, 1956.

(15) C. P. Smyth and C. S. Hitchcock, *J. Am. Chem. Soc.*, **54**, 4631 (1932).

(16) Ref. 3, Chap. II.

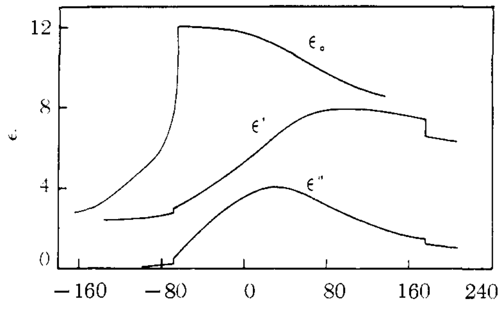

Fig. 3.—Static dielectric constant, ϵ_0, and dielectric constant, ϵ', and loss, ϵ'', at 3.19 cm. wave length as a function of temperature for *dl*-camphor.

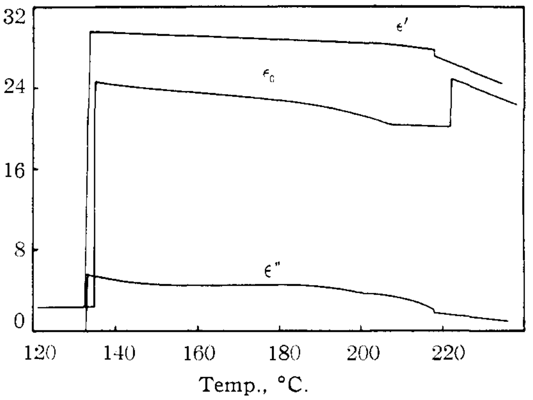

Fig. 4.—Static dielectric constant, ϵ_0, and dielectric constant, ϵ', and loss, ϵ'', at 3.19 cm. wave length as a function of temperature for *d*-camphoric anhydride.

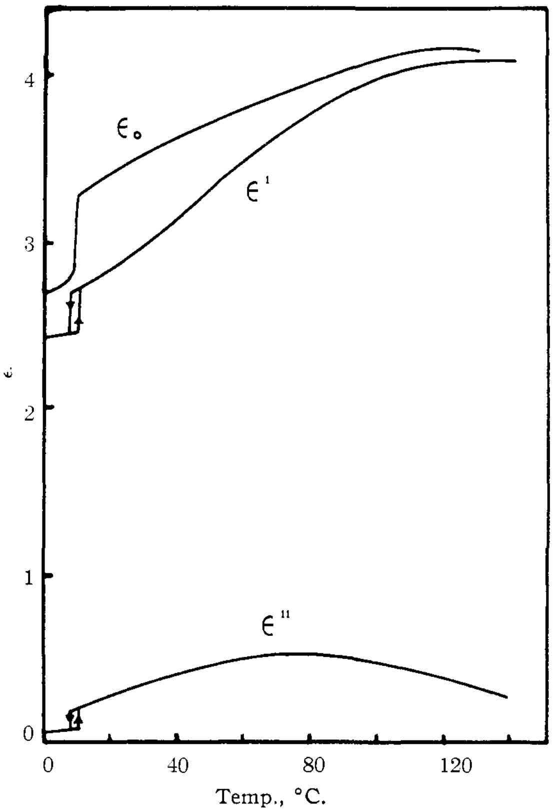

Fig. 5.—Static dielectric constant, ϵ_0, and dielectric constant, ϵ', and loss, ϵ'', at 3.19 cm. wave length as a function of temperature for *dl*-isoborneol.

dielectric constant of the solid rises like that of a polar liquid with decreasing temperature until molecular rotational freedom disappears sharply at a transition point, which shows a considerable hysteresis. The loss is considerable throughout the rotator phase, but, at the transition point, it drops, as it should, to a value so small as to be attributable to amplifier noise. It has been observed[17,18] that there is a phase change from cubic to rhombohedral at 97°, but there is no evidence in any of the curves in Fig. 2 that this change alters the molecular freedom in the crystal lattice.

The curves for *dl*-camphor (Fig. 3) resemble those for *d*-camphor in general form. The principal dispersion has almost ceased at 3.19 cm. when the temperature has decreased to that of the rotational transition. Below this temperature, a small, but appreciable dispersion is found at about −140° at a frequency of 1 kc. and at about −120° at 100 kc. The dielectric relaxation corresponding to this small absorption is too slow to produce appreciable loss at the very high frequency of the 3.19 cm. wave.

The static dielectric constant curve for *d*-camphoric anhydride in Fig. 4 is too low, probably, because the sample was melted into the cell and was less uniform and compact than the pressed sample used for the 3.19 cm. measurement. The very high dielectric constant is the result of the large dipoles pointing out from one side of the molecule. The changes in the 3.19 cm. dielectric constant and loss at the freezing point are almost negligibly small. Both the dielectric constant and loss increase slightly with decreasing temperature, but neither goes through the maximum commonly observed. The sharp drops in both the dielectric constant and the loss curves at the rotational transition indicate the disappearance of molecular rotational freedom at this temperature.

The measurements on *dl*-isoborneol (Fig. 5) could not be extended to the melting point because of the rapidity of its sublimation. In the temperature range covered both of the dielectric constant curves decrease with decreasing temperature to a rotational transition, below which the low frequency curve is enough higher than the 3.19 cm. curve to indicate the persistence of a small amount of hindered dipole orientation, possibly rotation of the hydroxyl group about its C–O bond. The loss curve goes through a maximum as observed for the other substances except the anhydride.

Dibromodichloroethane gave a dielectric constant curve at 3.22 cm. very similar to that obtained[19] at 5 kc., showing two transitions, the lower one involving complete disappearance of dipole orientation and accompanying loss. As careful examination of the effect of volume change showed that the latter completely altered the shape of the 5 kc. curve,[19] which was very sensitive to volume because of the

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(17) F. Wallert, *Compt. rend.*, **158**, 597 (1914).

(18) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **52**, 91 (1916).

(19) R. C. Miller and C. P. Smyth, *J. Am. Chem. Soc.*, **79**, 20 (1957).

low polarity of the molecule, it seems unnecessary to reproduce the observed 3.22 cm. curve here. The small loss at 3.22 cm. did not pass through a maximum with decreasing temperature but dropped to zero at the rotational transition point, at which the dielectric constant dropped to a value indistinguishable from the optical dielectric constant.

These molecules are all sufficiently close to spherical in form to permit rotational orientation over a considerable range of temperature. Because only one high frequency point is available, the arc plots are approximate, but the linearity of the plots of the logarithm of the relaxation time obtained from the arc against the reciprocal of the temperature gives significance to the values of the heat and entropy of activation calculated from the slope of the plot. The distribution parameter α, necessarily very approximate, decreases with rising temperature, as it does for liquids, but the change is greater than in the case of liquids, since α has a considerable value at low temperatures and decreases with rising temperature to zero far below the melting point. The heats and entropies of activation are of the same magnitude as those obtained for liquids, for example, those found for solutions in the very viscous Nujol.[20] It happens that the heat of activation for dielectric relaxation found[20] for *d*-*l*-camphor in Nujol was 2.42 kcal./mole as compared to the value 2.6 reported for the solid in Table I. The measurements on *d*-camphoric anhydride and dibromodichloroethane at 3.2 cm. wave length were somewhat removed from the very short critical wave lengths of these substances and, therefore, did not give sufficiently accurate values of the critical wave length to justify calculation of the heat and entropy of activation.

The molecules of these camphors and camphor derivatives are so similar in size and shape that they would be expected to have rather similar relaxation times.

This is broadly true, but the activation energy of *dl*-isoborneol is rather high and that of *dl*-camphene low. From dipole moment or polarizability considerations, isoborneol should have an activation energy lower than that of *dl*-camphor. On the other hand, hydrogen bonding if present should markedly increase the activation energy. Measurements carried out with this in mind showed that the infrared —OH band of a thin pressed sample of *dl*-isoborneol was shifted as it would be by hydrogen bonding. The low activation energy of the *d*-*l*-camphene as well as the negative entropy of activation would seem to imply that cooperative relaxation is less important in this case than for *dl*-camphor. The smaller dipole moment would also decrease the energy of activation, but the decreased interatomic distances of the body-centered cubic lattice of *dl*-camphor[21] would tend to increase the activation energy. The relaxation times for *dl*-camphor in solution in Nujol[20] are 17.5 × 10^{-12} sec. at 20° and 9.3 × 10^{-12} at 60°, very close to the values for the crystalline solid in Table I, 21.3 at 20° and 12.2 at 60°. The relaxation times of camphor in solution in several much less viscous solvents having viscosities from 0.37 to 0.97 centipoise have been found[22] to range from 5.8 to 10.7 × 10^{-12} sec. at 20°, not paralleling the viscosities.[20]

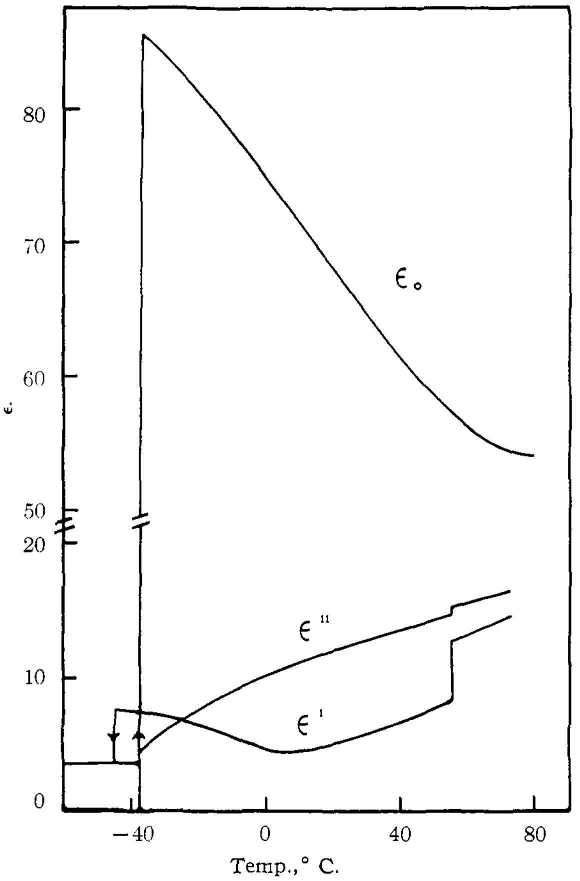

Fig. 6.—Static dielectric constant, ϵ_0, and dielectric constant, ϵ', and loss, ϵ'', at 3.19 cm. wave length as a function of temperature for succinonitrile.

The short critical wave length and relaxation time obtained for dibromodichloroethane in the solid state at 20° are slightly shorter than the values 0.65 cm. and 3.5 × 10^{-12} sec. obtained by extrapolation of measurements on the liquid from 25° down to 20°.[23] Several other tetrasubstituted methanes have been found[5] to show relaxation times of the same magnitude or shorter in the solid state than in the liquid, which means that the internal friction or viscosity hindering molecular rotation is of the same magnitude or less in the crystalline solid than it is in the liquid.[24]

A sharp transition from high to low dielectric constant of the type referred to in this paper as a rotational transition was observed in succinonitrile, $NCCH_2CH_2CN$, by White and Morgan.[8] van de Vloed[25] failed to find the transition and criticized the work of White and Morgan because the freezing point of their material was 54.2° instead of 57.2°. We found that the freezing point of the material varied with the method of purification. A sample recrystallized from acetone melted at 54.5°, while

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[20] O. F. Kalman and C. P. Smyth, *J. Am. Chem. Soc.*, **82**, 783 (1960).

[21] C. Finback, *Arch. Math. Naturwidenskat*, **B42**, No. 1, p. 77.

[22] D. H. Whiffen, *Trans. Faraday Soc.*, **46**, 130 (1950).

[23] R. C. Miller and C. P. Smyth, *J. Chem. Phys.*, **24**, 814 (1956).

[24] C. P. Smyth, *J. Phys. Chem.*, **58**, 580 (1954); *Proc. Natl. Acad. Sci. U. S.*, **42**, 234 (1956); *J. Phys. Chem. Solids*, **18**, 40 (1961).

[25] A. van de Vloed, *Bull. soc. chim. belg.*, **48**, 229 (1939).

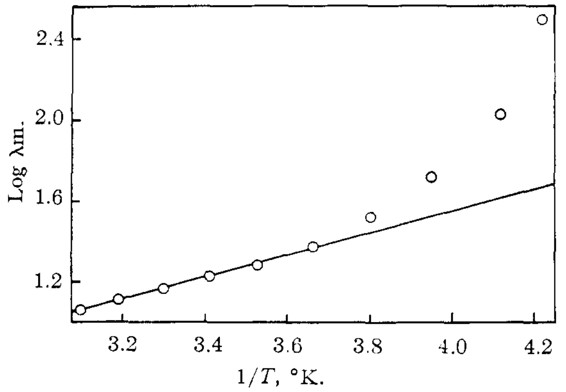

Fig. 7.—Logarithm of the critical wave length, λ_m, as a function of the reciprocal of the absolute temperature.

material distilled under vacuum melted at 57.2°. Although the measurements discussed in the present paper were made on samples melting at 57.2°, they confirm the presence of the transition (see Fig. 6), as do more recent measurements.[26] Our measurements carried out at 3.19 cm. gave the following critical wave lengths and relaxation times calculated by the method of arc plots from the data shown in Fig. 6.

TABLE II

CRITICAL WAVE LENGTHS, RELAXATION TIMES, AND HEATS AND ENTROPIES OF RELAXATION OF SUCCINONITRILE

Temp., °C.	λ_m (cm.)	$\tau(10^{-12}$ sec.)	Temp., °C.	λ_m (cm.)	$\tau(10^{-12}$ sec.)
−36.6	319	1695	10	19.1	101
−30	106	566	20	16.9	89.7
−20	51.4	273	30	14.7	78.0
−10	33.2	176	40	13.0	69.0
0	23.5	125	50	11.4	60.5

$\Delta H^{\ddagger}$, 2.5 kcal./mole; $\Delta S^{\ddagger}$, −6 e.u.

When the logarithm of the relaxation time is plotted against the reciprocal of the absolute temperature, the points above 0° lie closely on a straight line, but, as the temperature falls below 0°, rapid increase in the relaxation time causes increasing departure from linearity (Fig. 7). The values of the heat and energy of activation calculated from the slope of the straight part of the curve are in satisfactory agreement with the values $\Delta H^{\ddagger} = 2.1$ and $\Delta S^{\ddagger} = -4.8$ obtained by Clemett and Davies[26] from measurements at frequencies below 910 megacycles. The relaxation times in Table II are somewhat higher than those obtained by Clemett and Davies, 61×10^{-12} at 25.5°, 49×10^{-12} at 39.8° and 43×10^{-12} at 50°. This discrepancy, as well as the departure of the low temperature values of the relaxation time from linearity, may be the effect of a distribution of relaxation times increasing rapidly with decreasing temperature.

The relaxation of succinonitrile is peculiar. The body-centered cubic crystal in which succinonitrile is found[27] requires the molecule to have cubic symmetry. The other molecules studied have the symmetry as the result of rotation. The succinonitrile molecule is not spherical. It is rather closer in shape to a rod or a disk, depending on whether it is in the *trans* or *gauche* configuration. Moreover, the molecule would rotate as a whole in the latter only with great difficulty. The crystal lattice would allow spheres of only 2 Å. radius[27] while a sphere of 3.5 Å. is required to circumscribe the molecule. An average azimuthal angle of 80° between the two CN groups is estimated from the dipole moment calculated by means of the Onsager equation from the dielectric constant and density of the liquid at the freezing point. This is close to what would be expected for an equal mixture of the *trans* and *gauche* forms. All these data suggest that a combination of inter- and intramolecular rotation is taking place in succinonitrile. The activation energy for intramolecular rotation[28] is 1.2 kcal. compared to the value of 2.5 kcal. measured in the rotator state. The rapid increase in the relaxation time at low temperature mentioned above could then be due to a decrease in the amount of intramolecular rotation. The negative entropy of activation is consistant with such a special requirement as a combined intramolecular and molecular rotation.

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(26) C. Clemett and M. Davies, *J. Chem. Phys.*, **32**, 316 (1960).

(27) C. Finback and H. Vievoll, *Tids. Kjemi Bergvesen*, **2**, 35 (1942).

(28) G. L. Lewis and C. P. Smyth, *J. Chem. Phys.*, **7**, 1085 (1939).