low-up reaction, the base cannot have the role assigned to it in the iodination of aniline. What the function of the base is cannot be decided on the basis of the kinetic data alone, but another interpretation of the results is possible. Because of the acid-base equilibria of the buffer constituents, the kinetic data are also in agreement with an acid catalyzed reaction of hypoiodous acid and aniline with a possible transition state as shown in Fig. 3. The rate expression

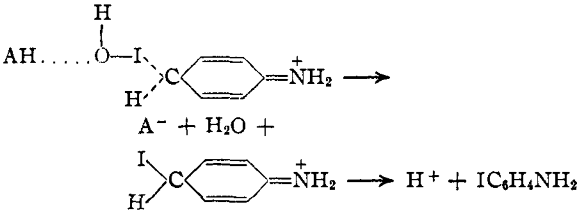

Fig. 3.

would then be $dx/dt = k_0[H^+][HOI][C_6H_5NH_2] + k'[HA][HOI][C_6H_5NH_2]$, and the role of the acid might consist in weakening, through hydrogen bonding, the oxygen–iodine bond of hypoiodous acid. The "water reaction" of I^+ and aniline would be identical with a reaction of hypoiodous acid and aniline catalyzed by hydrogen ions ($k_{obs.} = k_7K_1K_2/[I^-]^2$), and the base catalyzed reaction of I^+ would become the general acid catalyzed reaction of hypoiodous acid. The complex of hypoiodous acid and an acid can be described as a "solvated I^+," so that the iodinating agent can still be the I^+ ion, although the role of the base is different.[18]

A distinction between the two possibilities cannot be made until more is known about the transition state in aromatic substitution.

Acknowledgment.—I gratefully acknowledge the help afforded by a Frederick Gardner Cottrell Grant of the Research Corporation.

Summary

The kinetics of the iodination of aniline in water were studied in the presence of iodide ions and at different hydrogen ion concentrations. The reaction shows general base catalysis, and the kinetics are in agreement with a mechanism involving the positive iodine ion as the iodinating agent of free aniline.

An alternate mechanism involves an acid catalyzed reaction of aniline and hypoiodous acid.

[18] I am indebted to the Referees for calling my attention to the Note of Melander and to one of them for suggesting the alternate interpretation of the results.

BRYN MAWR, PA. RECEIVED JANUARY 27, 1950

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Heat Capacities, Dielectric Constants and Molecular Rotational Freedom in Solid Trichloroethanes and Disubstituted Propanes[1]

BY ROBERT W. CROWE AND CHARLES P. SMYTH

A number of substances whose molecular shapes are not far from spherical have been found to show polymorphism, the solids apparently possessing molecular rotational freedom for some distance below the melting points. Dielectric constant measurements have given evidence of this in 2-chloro-2-methylpropane,[2] 2-bromo-2-methylpropane,[2] 2,2-dichloropropane[3] and 1,1,1-trichloroethane[3] among others. It has been shown[4] that the molecular rotation in the solid leads to an abnormally high melting point. Although the liquid range of 1,1,2-trichloroethane, 151°, is somewhat larger than that of 1,1,1-trichloroethane, 107°, its rather high melting point, −36.0°, suggested that this substance also might possess some molecular rotational freedom in its crystal lattice. Simultaneous heat capacity and dielectric constant measurements or dielectric constant measurements alone were, therefore, made upon these substances and upon other compounds containing different groups attached to a central carbon atom. The measurements were carried out with an apparatus and method which have been previously described.[5]

Purification of Materials

1,1,1-Trichloroethane and 1,1,2-Trichloroethane.—Both compounds, obtained from the Eastman Kodak Company, were washed twice with 6 *N* sodium carbonate solution and with several portions of distilled water. They were then dried over anhydrous calcium chloride for twenty-four hours and fractionally distilled repeatedly at atmospheric pressure in a five-foot column. The physical constants of these compounds are

	This research			Literature		
	M. p., °C.	B. p., °C.	$n^{20}D$	M. p., °C.	B. p., °C.	$n^{20}D$
1,1,1-Trichloroethane	−33.0	74.0	1.4373	−32.7[3]	74.0[3]	1.4379[3]
1,1,2-Trichloroethane	−36.0	113.6		−36.7[6]	113.5[6]	

1,3-Dibromopropane.—Material from the Eastman Kodak Co. was washed several times

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

[2] Baker and Smyth, THIS JOURNAL, **61**, 2798 (1939).

[3] Turkevich and Smyth, *ibid.*, **62**, 2468 (1940).

[4] Baker and Smyth, *ibid.*, **61**, 1695 (1939).

[5] Kushner, Crowe and Smyth, *ibid.*, **72**, 1091 (1950).

[6] "International Critical Tables."

with dilute sodium carbonate solution and, finally, with several portions of water. It was then fractionally distilled under reduced pressure; m. p. −34.5° as compared to −34.4° ("International Critical Tables").

2-Chloro-2-nitropropane.—This compound was kindly furnished by Dr. R. H. Ewell, then of Purdue University, several years ago and has been stored since that time in the dark in a sealed pyrex tube. It was first washed with sodium carbonate solution to remove any hydrochloric acid present and then several times with distilled water. It was then dried for twenty-four hours over anhydrous calcium chloride and carefully distilled under reduced pressure. A constant boiling fraction, b. p. 65° (40 mm.), was collected.

2,2-Dinitropropane.—This compound, a yellow, crystalline solid, was also obtained from Dr. Ewell. It was purified by crystallizing three times from ethyl alcohol. The final traces of alcohol were removed by heating the compound to just above its melting point at reduced pressure for several hours. No attempt was made to purify it further by distillation because of its possible explosive properties.

Experimental Methods and Results

As in previous measurements, the average error in measurement of the heat capacity is estimated to be ±0.5 cal./deg. mole. Several runs were made on each compound that was measured and the resulting data, listed in Table I, were found to be quite reproducible. Since the values of the dielectric constants were very high in many cases, it became necessary to switch an auxiliary condenser of known capacitance into the circuit in order to balance the bridge without running off the scale of the precision condenser. As a result, some of the highest values, especially

TABLE I

HEAT CAPACITIES AND DIELECTRIC CONSTANTS

t, °C.	ϵ' (50 kc.)	C_p, cal./deg. mole	t, °C.	ϵ' (50 kc.)	C_p, cal./deg. mole
1,1,1-Trichloroethane					
−156.0		18.1	−63.5		30.0
−151.0		18.2	−60.0		32.5
−147.5		19.0	−58.5	2.54	
−143.0		19.1	−57.0		35.6
−141.0	2.20		−55.5	2.60	
−139.0		19.8	−54.0		41.5
−135.0		19.7	−53.0	2.65	
−131.0		20.2	−50.5	2.75	
−126.5		20.6	−49.0	2.86	
−122.5		20.6	−48.8	4.07	
−118.5		21.4	−48.5	5.62	
−115.5		21.7	−48.2	6.85	
−111.5		22.1	−47.8	7.55	
−108.0		22.5	−47.0	8.05	
−106.0	2.25		−45.8	8.40	
−104.0		22.9	−44.5	8.72	
−100.5		22.9	−42.0		40.3
− 97.0		23.1	−39.0	8.66	44.8
− 93.5		23.4	−35.7	8.75	
− 90.0		24.0	−33.5	8.75	
− 86.5		24.3	−30.0		32.9
− 83.0		24.6	−28.5	8.57	
− 81.5	2.30		−27.5		33.1
− 80.0		25.2	−26.0	8.45	
− 76.5		25.3	−24.5		33.0
− 73.0	2.36	27.0	−21.5		33.1
− 70.0	2.40	32.1	−20.0	8.26	
− 67.0	2.48		−18.5		33.1
− 66.5		32.8	−16.0		33.2
− 65.7	2.48		−14.5	8.19	
1,1,2-Trichloroethane					
−156.0		16.9	−70.0		29.1
−151.0		17.3	−66.5		29.4
−147.5		18.1	−63.5		30.0
−143.0		18.1	−61.8	2.61	
−139.0		18.8	−60.0		29.9
−135.0		19.1	−57.0		30.3
−132.8	2.47		−55.5	2.63	
−131.0		19.8	−54.0		30.6
−126.5		20.2	−51.0		30.8
−122.5		20.9	−49.3	2.65	
−118.5		22.0	−48.0		31.5
−115.5		22.6	−45.0		34.7
−113.5	2.49		−43.4	2.72	
−111.5		23.3	−42.0		42.0
−108.0		24.0	−40.5	2.77	
−104.0		24.6	−37.3	3.05	
−100.5		25.2	−36.6	3.60	
− 97.0		25.7	−35.7	8.45	
− 93.5		26.3	−35.4	8.77	
− 91.5	2.51		−35.3	9.22	
− 90.0		26.8	−33.0		33.6
− 86.5		27.4	−30.0		34.1
− 84.7	2.53		−28.6	9.00	
− 83.0		27.8	−27.5		34.4
− 80.0		28.2	−24.5		34.0
− 78.0	2.55		−23.0	8.78	
− 76.5		28.6	−21.5		34.2
− 73.0		28.9	−20.2	8.65	
1,3-Dibromopropane					
−156.0		18.8	−73.0		25.9
−151.0	2.45	18.7	−70.0		26.2
−147.5		18.9	−66.5		27.2
−143.0		19.1	−63.5		27.5
−139.0		19.2	−60.0	2.55	28.5
−135.0		19.8	−57.0		29.2
−131.0		19.8	−54.0	2.60	30.2
−126.5	2.47	20.2	−51.0		31.3
−122.5		20.6	−48.0		32.5
−118.5		21.2	−45.0	2.65	33.9
−115.5		21.2	−42.0		35.8
−111.5		21.6	−41.3	2.75	
−108.0		21.8	−38.9	2.86	
−104.0		22.5	−37.8	3.06	
−100.5	2.49	22.8	−36.7	3.50	
− 97.0		23.0	−36.5	3.95	
− 93.5		23.4	−36.2	4.65	
− 90.0	2.51	23.6	−35.9	5.27	
− 86.5		24.3	−35.5	6.32	
− 83.0		24.4	−33.7	11.05	
− 80.0		24.6	−30.0		37.0
− 76.5	2.53	25.1	−27.5	10.96	37.3

TABLE I (*Continued*)

t, °C.	ε′ (50 kc.)	*t*, °C.	ε′ (50 kc.)	*t*, °C.	ε′ (50 kc.)
2-Chloro-2-nitropropane (Cooling)					
−14.0	25.40	−27.3	30.70	−59.2	27.00
−19.3	26.52	−30.7	30.60	−59.3	23.85
−21.5	30.02	−33.9	30.35	−59.3	11.50
−21.7	30.70	−38.6	29.92	−59.5	4.30
−22.8	31.90	−40.4	29.85	−59.6	4.10
−23.3	31.80	−46.9	29.67	−61.6	3.65
−23.7	31.42	−50.1	29.64	−64.1	3.25
−24.1	31.00	−53.0	29.65	−69.7	2.94
−25.1	30.70	−58.7	29.67	−70.9	2.90
(Warming immediately)					
−70.4	2.82	−54.2	27.90	−22.2	30.38
−64.5	3.00	−50.4	28.70	−21.7	29.85
−59.0	4.25	−46.5	29.38	−21.5	29.40
−58.0	6.40	−40.8	30.23	−21.3	29.00
−57.4	15.42	−33.0	31.20	−21.1	28.47
−57.3	22.90	−29.1	31.55	−20.9	27.90
−57.2	27.11	−25.3	31.38	−18.6	26.88
−57.1	27.30	−23.3	30.88		
(Warming after 24 hr. below transition point)					
−62.8	2.93	−47.5	26.25	−21.8	29.55
−60.9	3.22	−41.8	27.93	−21.6	29.34
−59.0	4.03	−35.9	29.50	−21.5	29.10
−58.0	5.74	−32.0	30.35	−21.4	28.86
−57.6	10.75	−26.2	31.10	−21.3	28.62
−57.4	20.55	−23.3	30.35	−21.1	27.97
−57.3	23.35	−22.4	30.30	−21.0	27.35
−56.1	23.85	−21.9	29.91	−19.6	26.60
−54.2	24.33				
2,2-Dinitropropane (Cooling)					
56.2	35.7	39.3	37.9	−6.8	28.75
53.3	36.3	20.6	34.3	−6.9	14.80
53.2	38.9	10.6	32.6	−7.3	4.56
53.0	40.7	1.7	32.0	−7.6	3.02
52.8	41.4	−5.2	31.80	−13.8	2.65
51.9	42.4	−8.3	31.70	−15.7	2.62
48.2	41.1				
(Warming)					
−33.5	2.43	−5.1	11.18	51.9	42.6
−23.6	2.43	−5.1	18.50	52.6	40.6
−10.7	2.60	−5.0	29.70	52.8	39.5
−5.7	2.65	2.9	31.30	53.0	37.7
−5.3	2.80	12.8	33.70	53.2	35.9
−5.2	3.23	24.5	36.3	55.2	35.7
−5.1	7.80	39.3	39.5	58.2	35.3

in the case of 2,2-dinitropropane, are less accurate and are reported only to the first decimal place. The values below 30, however, are never more than ±1% in error. Since measurements with decreasing temperature were made by blowing small quantities of liquid nitrogen into the lead block surrounding the cell and then waiting for temperature equilibrium to establish itself, these results may be slightly in error. The samples were allowed to warm of their own accord at an even rate and, therefore, the values obtained with increasing temperature are more accurate and probably more indicative of the trend of the dielectric constant with changing temperature. The average rate of warming was about 0.1° per minute. In the transition and melting regions the rate was decreased markedly due to the energy involved in these processes. Although some conductance was observed in the nitro compounds, it was thought to be a result of traces of ionic impurities. No unusual changes in conductance occurred during the entire range of the measurements. As in the cases of the other compounds, therefore, dielectric constant values are reported only at 50 kc.

Temperatures, heats and entropies of transition and fusion, as determined in several runs, are listed in Table II. Heat and entropy changes are given for 2-chloro-2-nitropropane, although the heat capacity values are not of sufficient accuracy to warrant reproduction, and approximate transition and melting points are given for additional substances whose purity does not warrant reproduction of the other data.

TABLE II

TEMPERATURES (°K.), HEATS (KCAL./MOLE) AND ENTROPIES (E. U./MOLE) OF TRANSITION AND FUSION

	T. p.	M. p.	ΔH_t	ΔH_f	ΔS_t	ΔS_f
CH_3CCl_3	205		0.05			
	223.6	240.1	1.78	0.45	7.92	1.85
$CH_2ClCHCl_2$		237.1		2.72		11.48
$CH_3CHClCH_2Cl$		171				
$Br(CH_2)_3Br$		238.6		3.50		14.7
$(CH_3)_2CCl(NO_2)$	213.8 215.7	251.6	2.28	0.32	10.69	1.27
$(CH_3)_2CBr(NO_2)$	234 239	256				
$(CH_3)_2C(NO_2)_2$	266.1 268.1	326				
$(CH_3)_2C(CH_2NO_2)_2$	276	345				
$(CH_3)_3CNO_2$	258	296.5				

Discussion of Results

The dielectric constants and heat capacities of 1,1,1-trichloroethane are plotted in Fig. 1 as functions of increasing temperature. Here the transition and melting points are clearly shown. At the rotational transition, the dielectric constant rises sharply to a high value indicating as much freedom of orientation as that existing in the liquid.

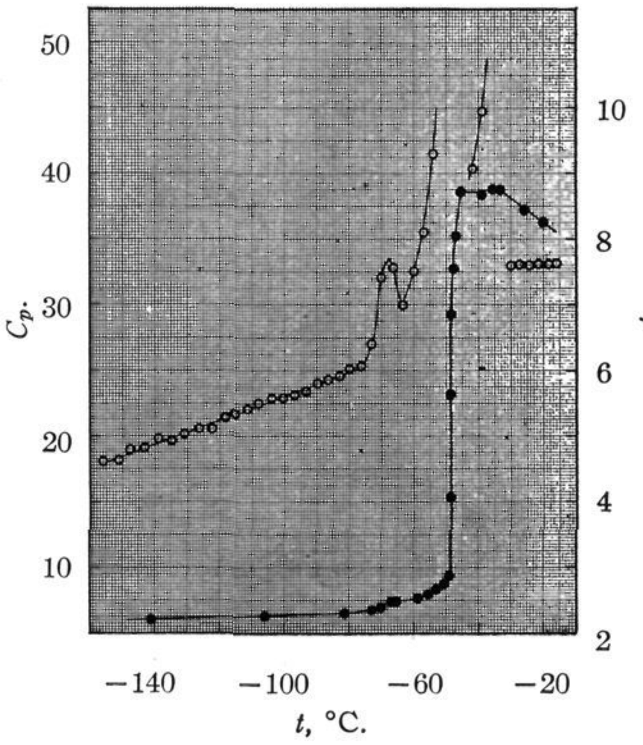

Fig. 1.—Temperature dependence of the dielectric constant and heat capacity of 1,1,1-trichloroethane. Filled circles represent dielectric constants and hollow circles heat capacities.

Since there is no apparent density change accompanying the melting process, it is somewhat difficult to determine the exact melting point. The small break and subsequent downward trend of the curve, however, indicate that the compound melts at about −33.0°. The transition temperature as determined from these measurements is −48.5°, a slightly higher value than that, −48.9°, reported by Turkevich and Smyth.[3] The region just below the transition point is of considerable interest. A small, very reproducible lambda point always appeared in the heat capacity curve with its peak at about −68°. At about the same temperature a small increase in dielectric constant also appeared. This increase is so small as to have been disregarded in the earlier investigation[3] in the absence of heat capacity data, but a close examination of the earlier data discloses a small break in the curve at the same temperature. The small lambda point in the heat capacity–temperature curve was observed previously for this compound[7] and attributed to a small amount of impurity which was believed to form a eutectic melting at this temperature. This belief was supported by the fact that an independent worker, Dr. E. A. Long, failed to observe the phenomenon with a different sample. Although the existence of a eutectic might well result in this type of heat capacity behavior, impurities, if present in very small amounts, usually cause a gradual rise in dielectric constant with rising temperature below the transition or melting point, accompanied by a corresponding increase in the slope of the heat capacity–temperature curve. Although the significance of the lambda point is not known, it appeared in all runs with this apparatus on this compound. It is of interest to note that a very small transition has been found just below the melting point of 1,1,1-trifluoroethane[8] with a heat of transition of 0.071 kcal./mole, as compared to 0.05 for that in 1,1,1-trichloroethane. The excessive rise in C_p between the lambda point and the true rotational transition, as well as the rise in dielectric constant in this region, may well be the result of increased librations of the molecules, as previously considered. The slight bending of the vertical portion of the dielectric constant curve in the transition region is probably the result of the somewhat rapid rate of warming necessary for the heat capacity measurements. Since the transition point and melting point of this compound are not far apart, the heat capacity values between the two points are extremely uncertain and obviously too high. This makes it difficult to estimate the energies involved in the two processes with accuracy.

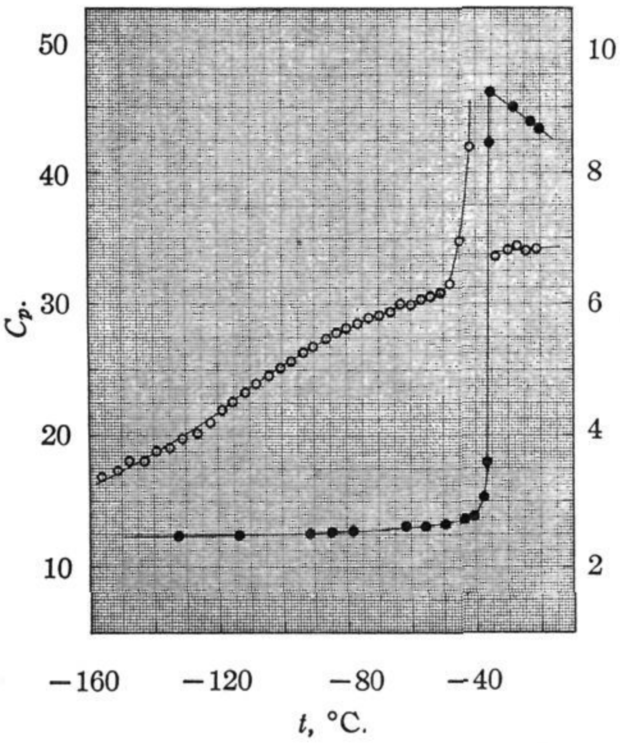

Fig. 2.—Temperature dependence of the dielectric constant and heat capacity of 1,1,2-trichloroethane. Filled circles represent dielectric constants and hollow circles heat capacities.

The combined heat capacity and dielectric constant data for 1,1,2-trichloroethane are plotted in Fig. 2. These measurements show no evidence of a rotational transition in the solid. The heat capacity rises normally to about 10° below the melting point and then begins to rise rapidly. This rise may be due to the presence of small amounts of impurity, but since the results were very reproducible even after successive distillations, the rapid rise in heat capacity and the gradual rise in dielectric constant may well be the result of the gradual onset of molecular rotational freedom below the melting point.[9] An examination of the molecular model of this compound shows that it is far from being as spherically symmetrical as 1,1,1-trichloroethane, and it is, therefore, not surprising that rotational freedom in the solid is not possible. Its structure may be compared with those of the ethylene halides. Both ethylene chloride and ethylene bromide have been shown to have transitions in the solid[10,11,12] which, at least in ethylene bromide, may be attributable to the onset of rotation of the molecules about the long axis in the *trans* position, thus having little effect on the dielectric constant. Evidently, replacement of one hydrogen atom by a chlorine atom so reduces the symmetry that rotation is not possible until the melting point is reached.

Rubin, Levedahl and Yost[7] list 1.786 kcal./mole and 0.45 kcal./mole for the heats of transition and fusion of 1,1,1-trichloroethane, in exact agreement with the values in Table II. The low heat and entropy of fusion is to be expected for this compound since rotation appears in the crystal at the phase transition and the molecules gain only translational freedom on melting. Since no

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[7] Rubin, Levedahl and Yost, THIS JOURNAL, **66**, 279 (1944).

[8] Russell, Golding and Yost, *ibid.*, **66**, 16 (1944).

[9] Smyth, *Trans. Faraday Soc.*, **42A**, 175 (1946).

[10] White and Morgan, *J. Chem. Phys.*, **5**, 655 (1937).

[11] Railing, THIS JOURNAL, **61**, 3349 (1939).

[12] Pitzer, *ibid.*, **62**, 331 (1940).

freedom of orientation exists in 1,1,2-trichloroethane until the melting point is reached, one must expect a much higher heat and entropy of fusion.

The dielectric constants and heat capacities of ethylene chloride have been remeasured in the course of the present investigation, but are not reproduced in this paper as their values are in adequate agreement with the results of the earlier measurements. In particular, the heat capacity values agree closely with the more accurate values of Pitzer[12] below the transition and throughout its course, but exceed Pitzer's values immediately below the melting point, where discrepancies are most apt to occur.

The heat capacities and dielectric constants of 1,2-dichloropropane have been measured, but some lack of reproducibility in the results makes desirable postponement of publication and detailed consideration of the data until further purification and more measurements have been carried out. It may, however, be reported that, like many other branched-chain molecules[13,14] it shows a strong tendency toward glass formation and no molecular rotation in the crystal.

The heat capacities and dielectric constants of 1,3-dibromopropane in Fig. 3 show no transition in the solid and no evidence of molecular rotation other than the possible trace commonly attributed to premelting. The five-atom molecular chain in the crystal can be regarded roughly as a cylinder with a diameter larger than the smallest diameters of the ethylene chloride and ethylene bromide molecules. The absence of rotation in the crystal is consistent with the absence observed in our investigations of alkyl bromide molecules of intermediate length[15] and of the longer bromides found by Hoffman and Smyth[16] to show no rotation until the 22-carbon molecule is reached.

The temperature dependence of the dielectric constant of 2-chloro-2-nitropropane is shown graphically in Fig. 4. This compound freezes into a solid rotator phase as indicated by the sharp increase in dielectric constant at the freezing point, $-21.5°$. This rise is undoubtedly the result of a considerable increase in density on solidification. The small peak just below the freezing point is probably due to momentary interfacial polarization. The dielectric constant soon drops slightly and remains nearly constant with decreasing temperature to the transition point. If true Debye behavior existed, the dielectric constant would rise with decreasing temperature as it does in the liquid. Negligible super-cooling was observed at the freezing and transition points. The transition occurred at $-59.3°$ as indicated by a sharp drop in dielectric constant to a value close to 4. With further decrease in temperature, the dielectric constant decreased slowly until it reached a relatively constant value of 2.80. On warming immediately, the transition occurred at a higher temperature, $-57.4°$, and the maximum value of the dielectric constant just above the transition was more than 3 dielectric units lower than that obtained on cooling. Also, instead of remaining nearly constant with temperature, it rose gradually above the transition. When the sample was allowed to warm up after being held several de-

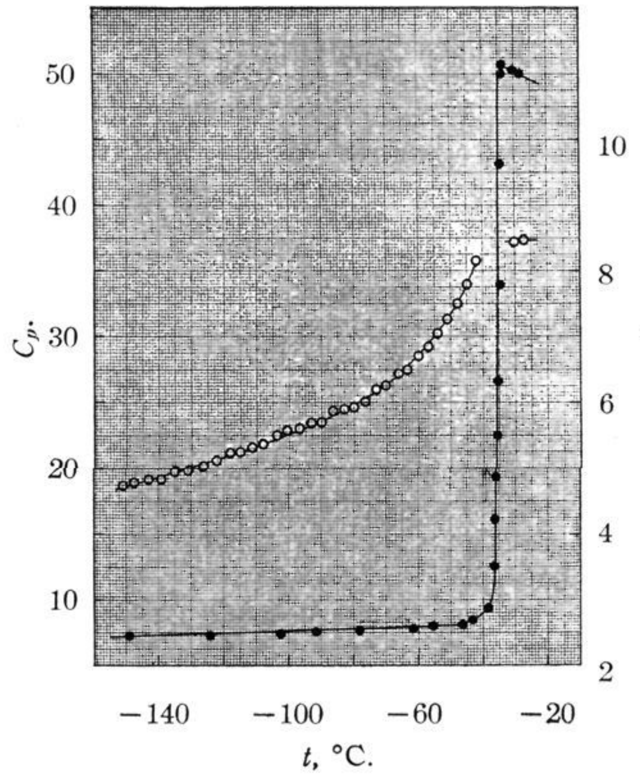

Fig. 3.—Temperature dependence of the dielectric constant and heat capacity of 1,3-dibromopropane. Filled circles represent dielectric constants and hollow circles heat capacities.

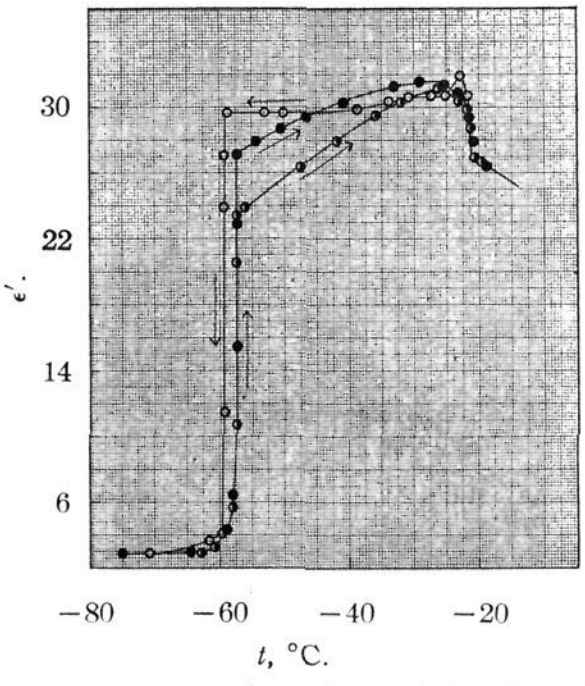

Fig. 4.—Temperature dependence of the dielectric constant of 2-chloro-2-nitropropane. Hollow circles represent values obtained with falling temperature, filled circles represent values obtained with rising temperature, and half-filled circles represent values obtained after the solid had been kept at low temperature for twenty-four hours.

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[13] Baker and Smyth, THIS JOURNAL, **61**, 2063 (1939).

[14] Turkevich and Smyth, *ibid.*, **64**, 737 (1942).

[15] Crowe and Smyth, *ibid.*, **72**, 1098 (1950).

[16] Hoffman and Smyth, *ibid.*, **72**, 171 (1950).

grees below the transition point for twenty-four hours, the maximum value of the dielectric constant just above the transition point was about 6 units below the value on the cooling curve. The slope of the curve with increasing temperature was even steeper and the values did not reach those of the cooling and first warming curves until the vicinity of the melting point was reached. The transition point, however, was exactly the same in both warming runs. The compound melted and froze at essentially the same temperature. From all appearances, the magnitude of the dielectric constant of the rotator phase was dependent upon the time that the temperature was held below the transition point. Since the number of molecules between the condenser plates in the cell cannot change appreciably after solidification, it must be assumed that orientation of the dipoles is somewhat restricted at lower temperatures. Prolonged low temperature treatment probably results in a tighter packing of the molecules in the lattice so that, after the transition takes place, the loosening of the lattice is not sufficient for the orienting dipoles to follow the Debye temperature relation. If this is the case, the increase in dielectric constant with rising temperature is evidently the result of increased ease of orientation brought about by thermal expansion of the lattice in this region.

Similar behavior to that observed here has been reported for other compounds. Baker and Smyth[2] observed a small hysteresis at the low temperature transition in *t*-butyl bromide. They also found that the dielectric constant increased with increasing temperature above this transition. A hysteresis has been found at the rotational transition in ethylene cyanide,[10] in certain camphor derivatives,[17] and at the low temperature transition in hydrogen sulfide.[18]

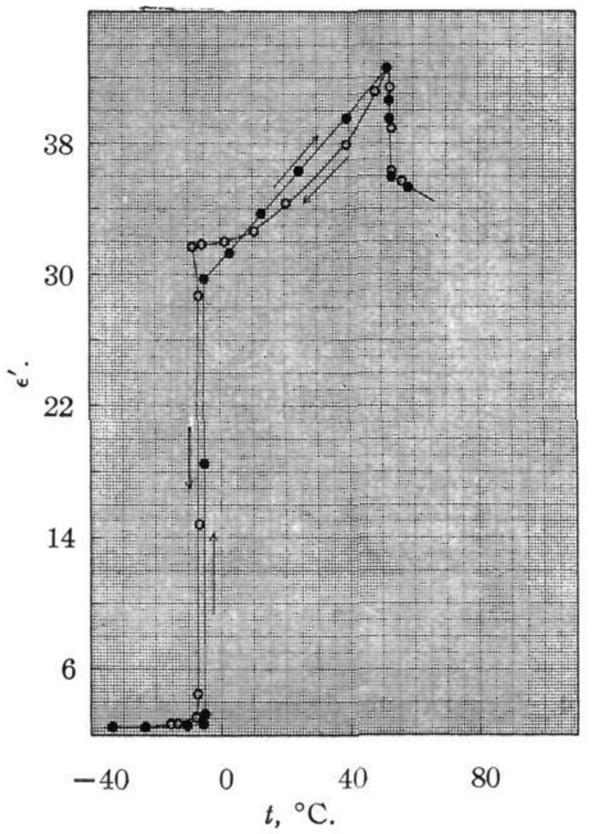

Fig. 5.—Temperature dependence of the dielectric constant of 2,2-dinitropropane. Hollow circles represent values obtained with falling temperature and filled circles represent values obtained with rising temperature.

The dielectric constant–temperature curves for 2,2-dinitropropane are shown in Fig. 5. The results obtained for this compound are quite similar to those obtained for 2-chloro-2-nitropropane, except that after the initial rise in dielectric constant on solidification, the values continued to decrease rapidly with decreasing temperature. As mentioned before, the irregular rate of cooling renders these values somewhat more uncertain than those obtained on warming. The point on the cooling curve at 20.3° was recorded after the sample had remained at that temperature for about twenty-four hours. This indicates that the dielectric constant of the rotator phase is not appreciably time dependent. The curve levels off slightly about 15° above the rotational transition. In contrast to the previously discussed compound, this compound super-cooled about 1.5° on cooling before the transition took place at −7.0°. However, similar hysteresis behavior was observed here, the transition appearing on warming at −5.0°. The dielectric constant attained a value close to 3.0 just below the transition and dropped to 2.50 at lower temperatures. From the warming curve it can be seen that the dielectric constant rises almost linearly with temperature above the transition, a phenomenon which is exactly opposite to that expected had Debye behavior occurred. Again it must be assumed that thermal expansion of the lattice with increase in temperature results in an increase in the freedom of orientation of the dipoles. The lack of the sharp peak in dielectric constant on cooling just below the freezing point, as well as the sharper melting and transition points, indicate that this compound was somewhat purer than the other compound investigated. In this case, prolonged cooling had no appreciable effect on the maximum value of the dielectric constant just above the transition point. Visual examination of these two nitropropanes in the crystalline rotator phase showed them to be almost transparent with a glassy appearance.

Because of difficulties in purification, the data on 2-bromo-2-nitropropane and dinitroneopentane are too inaccurate for reproduction. Both liquids froze to waxy solids, the high dielectric constants of which showed freedom of molecular orientation. The high dielectric constant, 30, of 2-bromo-2-nitropropane in the liquid state at the freezing point jumped to about 34 on solidification and rose to about 38 before the disappearance of rotational freedom at the transition point dropped it to about 4 and ultimately to 3.2 at −60°. The unusually large difference between the

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(17) Yager and Morgan, THIS JOURNAL, **57**, 2071 (1936).

(18) Smyth and Hitchcock, *ibid.*, **56**, 1084 (1934).

transition temperatures on cooling and on warming after twenty-four hours at low temperature may result from the presence of impurities. The conductivity of the sample of dinitroneopentane in the solid state near the melting point was too high for accurate measurement of the dielectric constant in this region. The dielectric constant, which was measured only with rising temperature, rose sharply from 3.2 at 0° and 4.0 at 3° to 18 at 4°, where the rotational transition was complete, and showed a gradual rise in the next 48°.

Previously unpublished measurements on 2-methyl-2-nitropropane carried out in this Laboratory some nine years ago by Dr. Willard P. Conner are consistent with the results on the closely-related substances which have just been discussed. Like the other nitropropanes, this material was obtained through the kindness of Dr. R. H. Ewell. As the substance is very difficult to obtain in a pure state, the first sample measured at a still earlier date in this Laboratory merely sufficed to show the existence of molecular rotational freedom in the solid state. A further purified sample gave the dielectric constant values plotted against temperature in Fig. 6. Although the freezing and transition points are sharp, the high maximum just below the freezing point may be attributed to the presence of impurities of relatively high conductivity, which give rise to interfacial or Maxwell–Wagner polarization with correspondingly high, apparent dielectric constant values. Although the dielectric constant values outside of this region of interfacial polarization are probably fairly accurate, it seems preferable not to tabulate them in this paper. However, the data in Fig. 6 show clearly that, in a temperature region extending some 39° below the freezing point, the molecules possess rotational freedom in the solid comparable to that in the liquid state.

The presence or absence of molecular rotational freedom in the crystalline states of the substances in Table II is consistent with the previously observed relation between molecular shape and rotational freedom. Neopentane, the *t*-butyl halides, 2,2-dichloropropane, 1,1,1-trichloroethane, and carbon tetrachloride have tetrahedral molecules so rounded at the corners as to have symmetries not far from spherical and thus are capable of rotation in the crystal.[2,3] The replacement of a chlorine in 2,2-dichloropropane by a nitro group raises the transition temperature by 26° and the melting point by 12°. The replacement of the remaining chlorine in 2-chloro-2-nitropropane by a second nitro group raises the transition temperature by 54° and the melting point by 74°, while replacement of the chlorine by bromine raises the transition temperature by 20° and the melting point by only 4°. Similarly, replacement of the chlorine in *t*-butyl chloride by a nitro group raises the transition temperature by 38.5° and the melting point by 48°, thus increasing the range of existence of the "rotator" state by 10°. Although the nitro group is not very different in size and shape from the methyl group and the halogens, its lower symmetry and high polarity should increase the difficulty of molecular rotation and thereby raise the transition temperature. The larger and more unsymmetrical $-CH_2NO_2$ group raises the transition temperature more, but, as it raises the melting point even more, the so-called "rotator" state exists over a longer range of temperature than in any of the other solids in Table II. The three substances in Table II which show no rotational transition points have molecules which depart so far from spherical form that packing in the crystal lattice prevents their rotation.

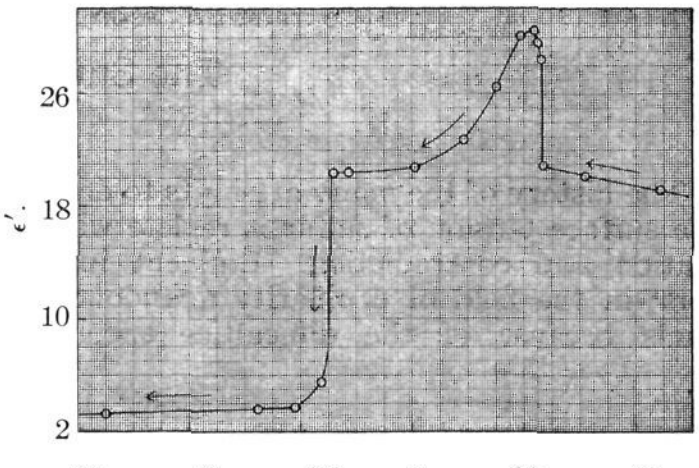

Fig. 6.—Temperature dependence of the dielectric constant of 2-methyl-2-nitropropane at 50 kc. with falling temperature (measurements by Dr. Willard P. Conner).

Summary

Simultaneous measurements of heat capacities and dielectric constants have been made with a combined heat conduction calorimeter and dielectric cell upon 1,1,1-trichloroethane, 1,1,2-trichloroethane, 1,2-dichloropropane, 1,3-dibromopropane, and 2-chloro-2-nitropropane from liquid nitrogen temperature to temperatures above the melting points of the solids. Dielectric constant measurements only have been made upon 2-bromo-2-nitropropane, 2,2-dinitropropane, and dinitroneopentane. Rotational transitions have been observed in 1,1,1-trichloroethane, 2-chloro-2-nitropropane, 2-bromo-2-nitropropane, 2-methyl-2-nitropropane, 2,2-dinitropropane, and dinitroneopentane, and in addition, a small lambda point has been found in 1,1,1-trichloroethane several degrees below the rotational transition. The molecules of these five substances have shapes sufficiently close to that of a sphere to permit rotational orientation in the crystal lattice over a considerable range of temperature below the melting point. The other three molecules examined are so unsymmetrical that packing in the lattice prevents their rotation.

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