

very widespread occurrence among ketones, because the enolization constant of acetoacetic ester (which is much more closely related structurally to the ketones studied by Nachod than is acetophenone), has been calculated from kinetic data for hydrochloric acid solutions from 0 to 0.370 molar,<sup>16</sup> and the values show no trend with increasing acidity.

### Summary

The iodination of acetophenone has been studied in 2 to 30% aqueous perchloric acid solutions, and in 0.5 to 66% aqueous sulfuric acid

(16) Pedersen, *J. Phys. Chem.*, **57**, 751 (1934).

solutions. The rate is determined by the rate of enolization of acetophenone in the more dilute acid solutions, and by the rate of reaction of the enol with iodine in 51% and more concentrated sulfuric acid solutions; at intermediate acidities these two rates are of comparable magnitudes.

Even in the simplest case, in aqueous perchloric acid solutions, the enolization rate is not proportional to  $h_0$ , but is proportional over a considerable range to  $c_{\text{OH}^+}$ . Reactions whose rates are directly proportional to  $h_0$ , when this is varied widely, are probably examples of specific hydrogen ion catalysis, and not of general acid catalysis.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

## Molecular Rotation and Polymorphism in the *t*-Butyl Halides

BY WILLIAM O. BAKER AND CHARLES P. SMYTH

A variety of roughly spherical molecules from methane to camphor is found to possess rotational freedom in the solid state, as well as polymorphic transitions at temperatures below which such freedom is generally lost.<sup>1,2</sup> The lower isomeric alkyl halides provide opportunity for studying the effect of structure on crystal form and molecular freedom in simple polar lattices by dielectric and optical measurements.<sup>3,4</sup> The tertiary butyl halides are the most symmetrical members of this series, and, despite their considerable dipole moments resulting from the dissimilar groups, they behave as spherical molecules in such a kinetic process as viscous flow.<sup>3</sup> Also, electron diffraction results on *t*-butyl chloride<sup>5</sup> indicate no appreciable distortion of the usual tetrahedral arrangement. The data of the present report on these compounds also may be compared with similar studies on the hydrogen halides.<sup>6-9</sup>

**Preparation and Purification of Materials.**—The final purification of the chloride and bromide was fractionation in an 80 × 2 cm. Pyrex glass column, packed with beads, wrapped, and jacketed. It had a still head equipped for reflux ratio control. Temperatures were measured by

short-range Anschütz type thermometers previously calibrated by the Bureau of Standards. The *t*-butyl iodide sample finally was distilled through a shorter Vigreux-type column under reduced pressure. Refractive indices were obtained from a Pulfrich refractometer. Immediately upon distillation the samples were frozen and kept in the dark until the dielectric measurements were begun.

***t*-Butyl Chloride.**—The compound was prepared by the method of "Organic Syntheses,"<sup>10</sup> from *t*-butyl alcohol and hydrochloric acid. The usual precautions of neutralization and washing were followed by prolonged drying over calcium chloride. The product was twice fractionally distilled; b. p. 50.60°; f. p. -24.6°;  $n_{\text{D}}^{20.0}$  1.38470. Material recrystallized from its own melt gave the same constants. Recent literature values give b. p. 51.0°,<sup>11</sup> and the refractive index noted above lies between the reported values 1.38528<sup>12</sup> and 1.3839.<sup>13</sup>

***t*-Butyl Bromide.**—As with the chloride, this compound was distilled from a mixture having the proportions of one mole of *t*-butyl alcohol and two moles of constant-boiling hydrobromic acid. After washing, it was dried for several days over anhydrous calcium bromide, and was thrice fractionated. Successive middle fractions had the same refractive index: b. p. 73.2°, f. p. -17.7°,  $n_{\text{D}}^{20.0}$  1.42757. A separately prepared lot gave the same refractive index, and boiled at 73.3°. The best literature values include: b. p. 73.25°,<sup>11</sup>  $n_{\text{D}}^{20}$  1.4275-1.4277.<sup>14</sup>

***t*-Butyl Iodide.**—The Eastman Kodak Co. product was distilled repeatedly under reduced pressure after thorough drying. Even though the best fractions came over colorless and were at once frozen, a light straw color always

- (1) Smyth, *Chem. Rev.*, **19**, 329 (1936).
- (2) Eucken, *Z. Elektrochem.*, **45**, 126 (1939).
- (3) Baker and Smyth, *THIS JOURNAL*, **61**, 1695 (1939).
- (4) Baker and Smyth, *ibid.*, **61**, 2063 (1939).
- (5) Beach and Stevenson, *ibid.*, **60**, 475 (1938).
- (6) Smyth and Hitchcock, *ibid.*, **55**, 1830 (1933).
- (7) Hettner and Pohlman, *Z. Physik*, **108**, 45 (1937).
- (8) Damkohler, *Ann. Physik*, **81**, 76 (1938).
- (9) Kruis and Kaischew, *Z. physik. Chem.*, **B41**, 427 (1939).

(10) Gilman, "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., 1928, Vol. VI11, p. 50.

(11) Timmermans and Delcourt, *J. chim. phys.*, **31**, 85 (1934).

(12) Smyth and Dornte, *THIS JOURNAL*, **53**, 545 (1931).

(13) Kistiakowsky and Stauffer, *ibid.*, **59**, 165 (1937).

(14) Kharasch and Potts, *ibid.*, **58**, 57 (1936).

developed in them, as was noted by Parts<sup>15</sup> also. However, if the samples were shaken with 1 cc. of pure mercury per 15 cc. of iodide, the sample became perfectly clear and could be distilled and preserved so. Indeed, liquid thus treated could be exposed to daylight for two days without noticeable discoloration, which suggests that minute traces of the decomposition products markedly accelerate the reaction. No reliable constants for this compound seem to be available in the literature. The melting point here found is  $-38.2^\circ$ .

#### Experimental Method and Apparatus

The dielectric measurements were made with a shielded capacitance bridge coupled to a General Radio Company low frequency variable oscillator and vacuum tube amplifier, and operated in the general fashion previously described.<sup>6,16</sup> The dielectric constant determinations for *t*-butyl bromide near and through the melting point were made at 520 kilocycles frequency with a heterodyne beat apparatus. Residual inductances introduced by the cell, which would cause its apparent capacity as measured by the bridge to vary with frequency, were found to be negligible by a calculation following a recently suggested scheme.<sup>17</sup>

All temperature measurements were made with a platinum resistance thermometer. Temperature control was by a metal block-Dewar tube assembly<sup>16,18</sup> of high heat capacity into which liquid air could be injected and evaporated at desired rates. Precautions were taken to ensure temperature equilibrium during runs, and to free the samples from gas bubbles by evacuation and slow, repeated freezing.

The compounds were examined from the liquid to low temperature crystalline states with a polarizing microscope, the arrangement in Fig. 1 being employed. Such optical examinations previously have been found useful in conjunction with other dielectric investigations,<sup>19</sup> and have been employed also by Kruis and Clusius to supplement X-ray data on hydrides.<sup>20,21</sup> In Fig. 1, T is an unsilvered Pyrex Dewar tube 11 cm. long by 3 cm. in diameter. It is held by clips on the microscope stage between the polarizer P and object lenses M. A low power lens gives adequate magnification, but for shorter focal distances an indentation in the side of T would permit closer approach of M to the drop of sample which rests on a glass slide S. The slide S is supported by a slotted cork section C at one end and by the stopper B at the other. It also rests on a glass tube A, through which liquid air may be injected in desired amounts to cool the sample through the freezing and transition points. I is a tube through which the sample is introduced, while V is a vent. Through V also may be passed the wires of a thermal element that may be sealed on the under side of S below the sample, and used to measure the temperatures of solidification, fusion and transition, although accurate determinations are unlikely in the simple system shown.

Observations with rising temperature are made by allowing the system to warm slowly, as the unsilvered Dewar permits. Under humid conditions, drying tubes are provided to prevent entrance and condensation of water vapor. Observations are conveniently made at least as low as liquid air temperatures. Such a scheme would seem to be of general use not only in preliminary investigations of solid state transitions, but also in rather striking visual demonstrations of transitions that are often found to cause large thermal, dielectric and density effects. The interpretation is by the usual polarizing microscope theory.<sup>22</sup>

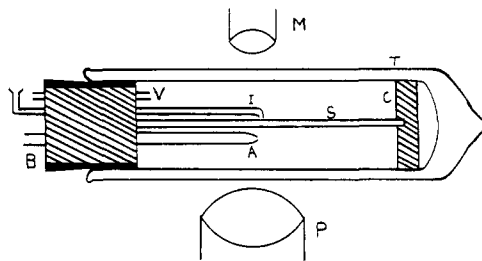


Fig. 1.—Vacuum-jacketed cell for use with polarizing microscope.

#### Experimental Results

The dielectric constants  $\epsilon$  and specific conductances  $k(\text{ohm}^{-1} \text{ cm.}^{-1})$  are listed in Table I with appropriate temperatures and frequencies. The readings were made in the time sequence 50, 5, 0.5 kc., so that when the dielectric constant was falling rapidly and isothermally at a freezing or transition point, the smaller number of dipoles left free to orient when the 0.5 kc. reading was made as compared to that present an instant before when the higher frequency readings were made caused the actual dielectric constant values to be higher at the higher frequency. The specific conductance values near the melting points and in the liquid probably contain some d. c. conductivity contribution. Both preliminary runs and duplicate measurements have been omitted for the sake of brevity.

#### Discussion of Results

The cooling curve for *t*-butyl chloride in Fig. 2 reveals a previously unreported thermal transition at  $-53.8^\circ$  whose latent heat considerably exceeds that of fusion. The variation of the dielectric constant with temperature is seen from Fig. 3 to resemble that of hydrogen chloride.<sup>6,7</sup> The portions of the curves obtained on cooling, however, slope downward with decreasing temperature while detailed results on the cooling behavior of hydrogen chloride are not available for comparison.

(22) Hartshorne and Stuart, "Crystals and the Polarizing Microscope," Edward Arnold and Co., London, 1934.

- (15) Parts, *Z. physik. Chem.*, **B7**, 327 (1930).  
 (16) Smyth and Hitchcock, *THIS JOURNAL*, **54**, 4631 (1932).  
 (17) Miller, *ibid.*, **60**, 42 (1938).  
 (18) Cone, Denison and Kemp, *ibid.*, **53**, 1278 (1931).  
 (19) Baker and Smyth, *ibid.*, **60**, 1229 (1938).  
 (20) Kruis and Clusius, *Physik. Z.*, **38**, 510 (1937).  
 (21) Kruis and Kaischew, *Z. physik. Chem.*, **B41**, 427 (1939).

TABLE I  
DIELECTRIC CONSTANTS AND SPECIFIC CONDUCTANCES

Kc. t, °C.		50		5		0.5		50		5		0.5		520		520		520						
ε		ε		ε		ε		ε × 10 <sup>9</sup>		ε × 10 <sup>9</sup>		ε × 10 <sup>9</sup>		ε		ε		ε						
												-29.5	14.18	14.20	14.32	38.5	1.7	0.7						
												-26.1	14.16	14.43	14.47	40.2	2.6	1.8						
												-25.4	14.08			35.2								
												t-C <sub>2</sub> H <sub>5</sub> Cl, Cooling						t-C <sub>4</sub> H <sub>9</sub> Br, Cooling						
8.0	10.54							1280						-28.3	13.81	14.09	14.38	83.4	13.0	7.2				
3.8		10.77						1120						-30.7	13.83	14.11	14.37	81.8	12.5	6.9				
3.3			11.78						1200					-32.0	13.85	14.13	14.36	83.4	12.1	6.8				
2.7	10.74	11.16	11.70	1260	1240	1240								-35.6	13.86	14.13	14.35	102.8	11.7	6.0				
1.8	10.84			1260										-39.3	13.91	14.16	14.34	102.8	10.3	5.3				
-6.2	11.36			1350										-41.9	13.95	14.20	14.37	117.4	9.7	5.0				
-8.4	11.53			1370										-44.9	14.04	14.28		122.2	9.1					
-9.2	11.57		11.61	1380				1350						-41.6			12.89			5.3				
-9.6	11.59			1380										-42.0	12.42			120.6						
-10.1	11.61			1400										-43.7		12.69	12.88		9.9	5.0				
-10.4	11.67			1390										-45.5	12.45	12.70	12.90	137.9	6.2	4.5				
-13.3	11.88			1300										-48.4	12.50	12.75	12.91	176.3	9.2	4.6				
-15.1	11.91			1280										-65.5	13.00	13.03	13.65	88.2	5.0	2.4				
-16.8	12.03			1280										-65.7		12.15	10.20		5.0	2.4				
-20.1	12.34			1280										-65.9	8.54	5.07	3.33	52.0	10.6	6.9				
-20.5	12.37			1280										-66.0	2.88	2.91	3.04	26.6	9.6	5.3				
-21.8	12.45			1280										-72.1	2.75	2.81		21.4	7.6					
-22.3	12.49			1280										-75.3			2.91			4.6				
-23.2	12.70			1250										-83.7	2.65	2.70	2.80	17.7	4.4	3.5				
-24.6	14.28			21.4										Warming										
-29.2	13.89			19.6										-118.5	2.42	2.42	2.40	1.4						
-31.6	13.79			17.7										-106.5	2.50	2.51	2.51	1.5						
-33.0	13.68			17.7										-100.2	2.61	2.62	2.62	1.5						
-35.0		13.69	13.77			3.5	1.6							-70.7	2.69	2.79	2.98	14.2	5.4	3.6				
-37.0	13.57	13.64	13.85	15.9		3.1	1.3							-68.1	2.71	2.84	3.08	17.7	7.1	5.0				
-38.6	13.57	13.68	13.89	14.2		3.0	1.3							-65.8	2.74	2.88	3.20	19.6	9.2	6.3				
-41.2	13.51	13.55	13.80	14.2		2.4	1.0							-64.5	2.79	2.97	3.25	23.1	8.4	5.8				
-46.3	13.39			8.9										-64.5	2.94	3.09	3.35	19.6	7.4	4.5				
-49.1		13.40				1.7								-64.4	3.24	3.41	3.70	17.7	5.3	3.3				
-51.3			13.52				0.8							-64.3	5.01	6.67	8.96	17.7	5.9	3.2				
-54.0	8.47	5.61	2.71	8.9	1.2	1.0								-64.2	11.79	11.97	12.07	23.1	6.0	3.3				
-53.8	4.03			14.2										-64.1	11.86	12.03	12.15	23.1	6.2	3.5				
-53.8	2.51	2.55	2.65	5.3	2.8	1.2								-63.6	11.88	12.06	12.17	23.1	6.5	3.5				
-53.8	2.46	2.50	2.54	5.3	2.7	1.2								-59.7	11.89	12.07	12.22	24.9	7.1	3.8				
-56.2	2.45	2.48	2.52	4.0	1.6	0.9								-55.4	11.90	12.10	12.27	28.3	7.6	4.2				
-60.0			2.52											-43.8	11.99	12.20	12.42	31.8	9.4	5.3				
-66.6	2.41	2.43	2.47	3.5	1.0									-42.4	11.99	12.23	12.44	33.5	9.6	5.3				
												Warming						Warming						
-69.3	2.53	2.56	2.58	0.1	0.1	0.1								-41.3	12.14	12.70	13.42	35.2	10.5	5.3				
-66.0	2.55	2.57	2.60	.1	.1	.1								-41.4	13.54	14.28	14.48	35.2	9.2	5.0				
-62.8	2.57	2.58	2.62	.1	.1	.1								-41.4	14.09	14.33	14.51	35.2	9.2	5.1				
-59.6	2.58	2.60	2.64	.1	.1	.1								-41.3	14.12	14.35	14.54	35.2	9.4	5.3				
-56.9	2.60	2.63		.1	.1	.1								-38.4	14.13	14.36	14.56	35.2	9.9	5.6				
-55.8			2.68											-25.8	14.17	14.45	14.74	45.2	14.2	8.6				
-53.8	2.63	2.67	2.83	.1	.6	.5								-25.0	15.03	16.06	17.41	162.0	41.5	23.6				
-53.5	3.08	5.36	9.45											-24.3	15.05	16.20	17.76	177.2	48.5	29.0				
-53.4	14.94			26.6										-23.6	15.11	16.66	18.28	219.5	65.0	37.3				
-53.4	15.02			26.6										-22.7	15.15	17.02	19.12	309.2	78.4	50.1				
-52.9	15.07			26.6										-21.1	15.26	18.89	21.87	523.3	139.4	99.2				
-52.2	14.97			26.6										Kc. t, °C.	520	Kc. t, °C.	520	Kc. t, °C.	520					
-51.2	14.95			26.6																				
-48.4	14.89			26.6																				
-46.8	14.82			45.2																				
-43.3		14.72	14.77		1.2	0.5																		
-39.4	14.55	14.54	14.62	45.2	1.2	.6																		
-36.0	14.38	14.40	14.50	45.2	1.6	.6																		
-34.0	14.32	14.34	14.44	45.2	1.8	.6																		
												Warming						Warming						
												-23.6	14.11	-18.7	13.87	-17.7	13.16							
												-22.7	14.11	-18.5	13.79	-17.6	12.62							
												-21.8	14.07	-18.4	13.73	-17.5	12.52							
												-21.0	14.03	-18.3	13.63	-16.9	12.48							
												-20.5	14.02	-18.1	13.56	-15.9	12.43							
												-20.0	14.02	-17.9	13.54	-14.7	12.37							
												-19.3	13.99	-17.8	13.53									

TABLE I (Concluded)

Kc. $t, ^\circ\text{C.}$	5	0.5	50	5 $k \times 10^{10}$	0.5
<i>t</i> -C <sub>4</sub> H <sub>9</sub> I, Warming					
-184.3	2.58	2.57	2.58	3.5	0.6
-149.7	2.60	2.60	2.65	3.5	.7
-141.4	2.64	2.65	2.70	7.1	1.4
-120.2	2.67	2.67	2.72	5.3	1.7
-107.0	2.68	2.68	2.87	8.9	4.7
- 87.9	2.72	2.86	3.61	28.3	17.5
- 83.0	2.73	2.96	4.08	38.5	25.0
- 79.2	2.74	3.74	7.50	122.2	75.5
- 72.6	2.80	4.45	9.01	200.0	112.8
- 68.4	2.88	4.91	9.24	258	142.0
- 62.2	3.13	5.40		347	268
- 59.2	3.25	5.70		428	258
- 55.3	3.47	6.21		512	348
- 52.9	3.65	6.52		669	430
- 50.7	3.83	6.82		802	534
- 45.6	4.20			1333	
- 44.0	4.67			1586	
- 43.3	4.73			1685	
- 40.9	3.12			2220	
- 39.4	5.81			2718	
- 39.2	6.25			2880	
- 39.1	6.36			2890	
- 39.1	6.45			2900	
- 39.0	6.62			2920	
- 38.9	6.90			2940	
- 38.8	7.12			2940	
- 38.2	10.13			2790	
- 38.2	10.50			2800	
- 38.2	11.22			2440	
- 38.2	11.09			2420	
- 38.1	11.12			2873	
- 38.0	11.04			2870	
- 38.0	10.99			2870	
- 34.3	10.61			2020	
- 33.7	10.61			1881	
- 33.4	10.47			1840	
- 32.6	10.45			1780	
- 32.2	10.44			1770	

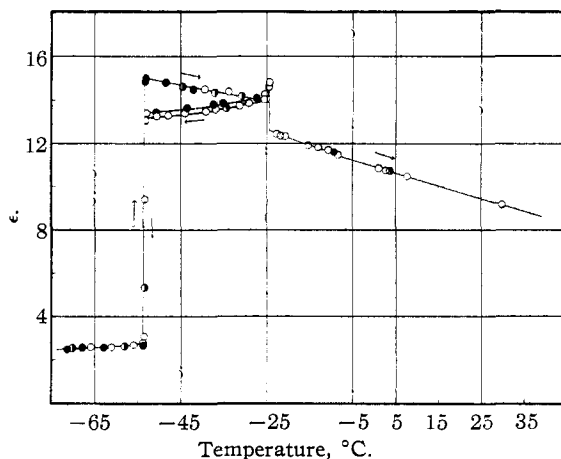


Fig. 3.—Temperature dependence of the dielectric constant of *t*-butyl chloride. (Hollow circles represent values at 50 kc., half-filled circles values at 5 kc., and filled circles values at 0.5 kc.)

The highest temperature point in the liquid on Fig. 3 was obtained independently<sup>12</sup> in a dipole moment study. On solidification the dielectric constant rises because of increase in density, shows a low sharp peak, presumably because of a small Maxwell-Wagner interfacial polarization, and then gradually declines with a small but definite dispersion. At the transition temperature, the dielectric constant drops sharply to a value near to the square of the refractive index, with disappearance of dispersion. The transition is shown by the polarizing microscope to be an enantiotropic transformation from a high temperature cubic to a low temperature form of lower symmetry. The abrupt lattice change into an anisotropic packing arrangement would follow from a cooperative interlocking of the dipoles when they had reached a sufficiently low temperature to lose most of their librational energy. Such a sharp interaction is indicated by Fig. 4, where the curve denoting the lower  $\epsilon''$  values in the region of  $-53.8^\circ$  rises steeply to a maximum just at the temperature of the transition. Hence, a rapid and widespread interference to orientation is introduced by a loss maximum, so narrow that it is only a straight line for 50 kc. at the peak. Then the dipoles are immobilized in the low temperature crystal form.

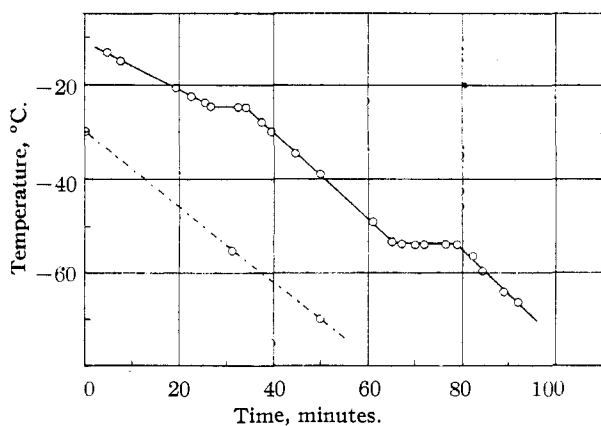


Fig. 2.—Temperature-time curve (cooling) for *t*-butyl chloride.

The dielectric constant curve obtained with rising temperature, shown by arrows on Fig. 3, exhibits a sharp ascent at the transition, which is unaccompanied by thermal hysteresis, to a value which declines on further warming, as expected from the Debye relation. If the co-

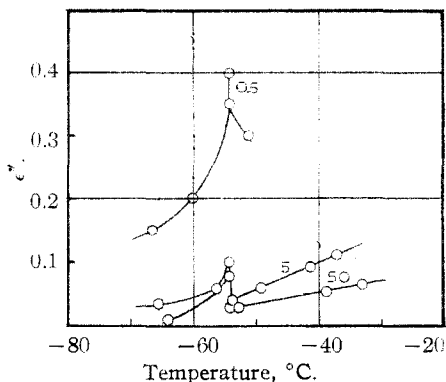


Fig. 4.—Temperature dependence of the imaginary part  $\epsilon''$  of the dielectric constant of *t*-butyl chloride.

operative<sup>23</sup> loosening of the molecules at the transition on warming is strong enough to give immediately the maximum orientational freedom of the cubic lattice, whereas, on cooling, a decrease in the molecular disorder probably existing immediately after solidification gradually reduces this freedom, the observed difference in the warming and cooling curves would be accounted for. Microscopic examination revealed qualitatively a considerable density increase on cooling through the transition.

Figure 5 contains the thermal arrests marking the two polymorphic transitions found for *t*-butyl bromide. The higher temperature transition, henceforth called I, is attended by supercooling but comparison of the heating and cooling curves, together with the dielectric results, indicates that it occurs without thermal hysteresis at  $-41.4^\circ$ .

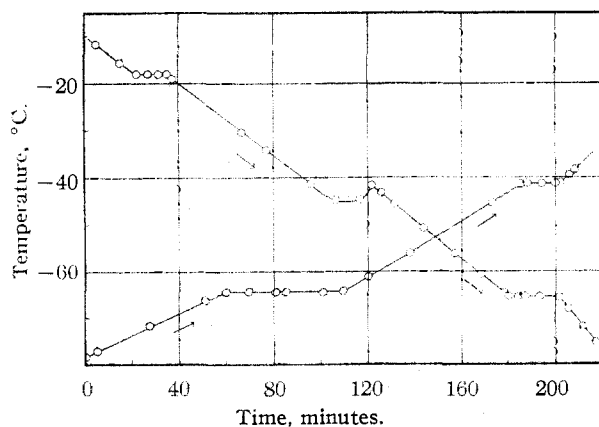


Fig. 5.—Temperature-time curves for *t*-butyl bromide.

The lower transition II shows no supercooling but occurs abruptly at  $-65.8^\circ$  on cooling, and at

(23) "Coöperative" is here and elsewhere taken from the usage of Fowler, "Statistical Mechanics," Cambridge University Press, Cambridge, England, 2d ed., 1936, Chap. 21.

$-64.2^\circ$  on warming. Evidently from Fig. 5 the heat of fusion is less than the heat of transition II, and much less than the sum of the heats of the two transitions.

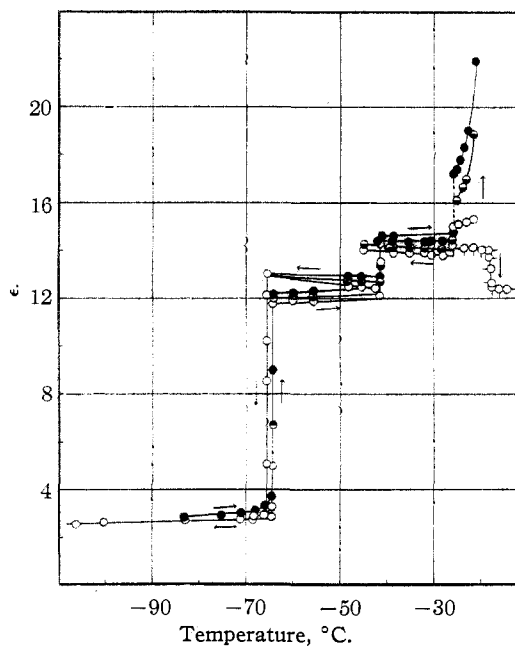


Fig. 6.—Temperature dependence of the dielectric constant of *t*-butyl bromide. (Hollow circles represent values at 50 kc., half-filled circles values at 5 kc., and filled circles values at 0.5 kc.)

An enhanced dispersion in the same frequency range results from replacement of a chlorine atom by the larger, more polarizable bromine, as demonstrated by Fig. 6. In some parts of the graphed data points at the three frequencies would have been superposed, so but one point was indicated, for example, the point immediately above transition II, on cooling. The data for the lower frequencies begin somewhat below the freezing point, for, just after solidification, bridge balancing became uncertain and large apparent dielectric constant values were obtained, probably because of interfacial polarization. This effect has been found by Yager and Morgan<sup>24</sup> for several camphor derivatives, and by White and Morgan<sup>25</sup> for ethylene cyanide, all of which possess rotational freedom in the solid. The effect here does not exceed a maximum apparent specific conductance of  $5 \times 10^{-8} \text{ ohm}^{-1} \text{ cm.}^{-1}$ , whereas they report values greater than  $10^{-6} \text{ ohm}^{-1} \text{ cm.}^{-1}$ . The values obtained at 520 kilocycles with a

(24) Yager and Morgan, *THIS JOURNAL*, **57**, 2071 (1935).

(25) White and Morgan, *J. Chem. Phys.*, **5**, 655 (1937).

heterodyne beat apparatus are shown through the melting point by the tagged circles.

The supercooling at transition I is expressed on the dielectric graph by an exact continuation of the curves for the highest temperature solid form some  $3^\circ$  below  $-41.4^\circ$ . Suddenly, the values revert back on just these lines, as far as could be determined experimentally, and the dielectric constant drops sharply at the transition to a new set of curves, which show diminishing dispersion with decreasing temperature. At  $-65.8^\circ$ , a transition like that in *t*-butyl chloride occurs. However, below this point for a short temperature interval there is still dispersion, apparent in the data but too slight to be evident in Fig. 6. As with the chloride, a sharp rise in  $\epsilon''$  marks the interaction introduced by transition II.

On warming, a slight rotational pre-melting, consonant with the suggestion of coöperative lattice loosening with rising temperature noted for *t*-butyl chloride, is followed by the onset of rotation, now at  $-64.2^\circ$ . This slight rotational freedom below a transition seems comparable to the pre-melting previously noted for many molecular lattices.<sup>19</sup> The latter behavior has been confirmed by X-ray and thermal analyses of highly purified hydrocarbons,<sup>26</sup> and has been given theoretical interpretation and justification by Frank's recent order-disorder treatment of melting.<sup>27</sup> It would seem that in a treatment of arrangement in terms of rotational disorder and of the corresponding lattice energy change dependent on the degree of such disorder, a transition state just below the observed transition temperature like that proposed by Frank just below the melting point would account for the experimental data.

The apparent  $1.6^\circ$  hysteresis in the temperatures of transition resembles the  $1.1^\circ$  difference in the case of the analogous transition in hydrogen sulfide,<sup>28</sup> the longer interval in ethylene cyanide,<sup>25</sup> and the less sharply defined hystereses in camphor and its derivatives.<sup>24</sup> The same hystereses are found in thermal measurements, and were thus discovered at the rotational transitions of methane and deuterated methane.<sup>29</sup>

Pressure studies by Clusius and Weigand<sup>30</sup> on the hydrogen sulfide transition reveal that it is

accompanied by a volume change of about 7.6%, and by a mean lattice separation change so small that it might remain undetected in X-ray photographs. However, easily obtainable pressures with hydrogen gas broadened the hysteresis range, and the hysteresis area was found to be smaller in deuterium sulfide. Hence, apparent hysteresis in these transitions would seem to be sensitively affected by changes in structure and environment. The apparent temperature of the monotropic transition in ethyl stearate was found to depend on the temperature gradient to which the sample was exposed.<sup>19</sup> This result was confirmed for other similar long chain compounds.<sup>31</sup> It provides evidence for the idea that critical fluctuations in  $\Delta F$  and  $\Delta S$  must occur for the progression of spontaneous solid transformations. This concept has been elaborated by Ubbelohde.<sup>32</sup> The activation entropies for rotation of even simple molecules in the solid state have been found to be very high.<sup>33</sup> Therefore, it is possible that the *t*-butyl bromide hysteresis occurs because, in order that transformation may be induced, the substance must be cooled slightly below the true equilibrium point to produce an enhanced thermodynamic potential. Then, the material may lose heat to the environment so readily that the temperature of the sample never rises to the equilibrium value, despite the relatively large latent heat. This agrees with the observation that the sample could be cooled under a larger gradient and made to lose heat so rapidly that the transition appeared to occur at  $-67.2^\circ$ . However, the process at  $-65.8^\circ$  as shown by Figs. 5 and 6 is not an ordinary supercooling like that at transition I.

A macroscopic potential, or tension, in the crystal mass produced by the transition has been suggested by Frank<sup>34,35</sup> as the possible cause of hysteresis. The rate of temperature change as the transition is approached should strongly influence the hysteresis, it would seem. Further limitations on this idea have been noted by Eucken.<sup>36</sup>

An explanation applicable to certain examples of hysteresis is suggested by the dielectric and thermal results on *n*-amyl bromide,<sup>3</sup> and by the X-ray studies of Wallerant on camphor.<sup>37</sup> The

(26) Ubbelohde, *Trans. Faraday Soc.*, **34**, 282, 292 (1938).

(27) Frank, *Proc. Roy. Soc. (London)*, **170**, 182 (1939).

(28) Smyth and Hitchcock, *THIS JOURNAL*, **56**, 1084 (1934).

(29) Kruis, Popp and Clusius, *Z. Elektrochem.*, **43**, 664 (1937).

(30) Clusius and Weigand, *ibid.*, **44**, 674 (1938).

(31) Vold and Vold, *THIS JOURNAL*, **61**, 808 (1939).

(32) Ubbelohde, *Trans. Faraday Soc.*, **33**, 1203 (1937).

(33) Baker and Smyth, *J. Chem. Phys.*, **7**, 574 (1939).

(34) Frank and Wurtz, *Naturwissenschaften*, **26**, 687 (1938).

(35) Frank, *Z. Elektrochem.*, **45**, 150 (1939).

(36) Eucken, *ibid.*, **45**, 150 (1939).

(37) Wallerant, *Compt. rend.*, **188**, 597 (1914).

latter found that, besides the cubic form existing above the transition, three less symmetrical classes occur at successively lower temperatures. Monotropic transitions below a rotational transition would produce the same effect on it as that of the *n*-amyl bromide transition in raising the melting point several degrees above the freezing point. A careful thermal and X-ray analysis of other substances showing hysteresis might establish such low temperature polymorphism.

Examination with the polarizing microscope showed *t*-butyl bromide to form a translucent, isotropic, definitely crystalline lattice on solidification, which was transformed enantiotropically at transition II to or from an opaque, birefringent, anisotropic lattice. Transition I was accompanied by no change in the cubic form, but, apparently, by a contraction on cooling and an expansion on warming. This is indicated by the migration of the Beeke line across the sample as it transforms. In a homogeneous medium, differences in refractive index, detected under the polarizing microscope by brightness variations with a constant source, result from density differences. At the vertical junction between a more dense phase B and a less dense one A,  $n_B > n_A$ , where  $n$  is the refractive index. The rays which pass from A to the denser medium B are bent toward the normal to the junction within B. Rays passing from B toward the junction which impinge within the critical angle are totally reflected and emerge on the B side. The result of these combined effects is to illuminate more brightly the B side of the junction. Here the junction is the interface between the transformed and untransformed material, and, at the transition point, a darkish line is seen to move across the sample. It is concluded that I is an enantiotropic lattice change shown by Fig. 5 to possess a latent heat and accompanied by a density shift which does not destroy the cubic arrangement.

The supercooling at transition I, shown on Figs. 5 and 6, is like that frequently observed at solid-liquid transitions. Thermal measurements on phosphine disclosed a low temperature rotational transition and an intermediate one,<sup>38</sup> analogous to those of *t*-butyl bromide. The intermediate transition in phosphine also shows supercooling, whereas the lower one, which presumably marks the end of librational freedom, does not, in agreement with the *t*-butyl bromide results. The di-

electric data provide a possible interpretation of the general property of supercooling in some polymorphic transitions, and its absence in others. Figure 5 indicates a much smaller latent heat for transition I than for transition II. The difference between the entropy changes at the two points is also large. A metastable condition of the solid phase which is stable above the temperature of transition I induced by cooling it somewhat below the transition temperature will be under a relatively small thermodynamic potential tending to force the transformation. Further, Fig. 6 indicates by the relatively small decrease in dielectric constant at transition I only a slight loss in orientational freedom of the dipoles. Hence, on cooling, the thermal agitation of the molecules which, at a given instant, have undergone the transition, will make them poor ordering centers for the cooperative formation of the lower temperature stable form. On the other hand, transition II, and, presumably also, as a dielectric study should reveal, the lowest transition in phosphine, marks the loss of most of the rotational molecular freedom. The molecules cease to exhibit nearly spherically symmetrical force fields, and become so definitely oriented that a rearrangement occurs, resulting in the formation of an anisotropic lattice. These effects are evidenced by the loss of orientational polarization seen in Fig. 6, and the large latent heat of the transition indicated in Fig. 5. The same causes account for the absence of supercooling at the transition in *t*-butyl chloride. Such considerations would seem generally adaptable to thermal studies of polymorphism in molecular and some ionic lattices. They are consonant with other ideas on the importance of orientation in supercooling.<sup>4</sup>

Figure 7 indicates the expected result that the least symmetrical most polarizable molecule of the series, *t*-C<sub>4</sub>H<sub>9</sub>I, interacts in the solid so strongly that it can rotate only with difficulty above the transition point  $-79.4^\circ$ . This hindrance effects the pronounced dispersion seen on the graph, but the dielectric loss, proportional to the tabulated apparent specific conductance, contains a considerable d. c. conductance contribution from impurities which could not be removed. The critical frequency of the rotating dipoles is probably near 50 kc., as the dielectric constant values for this frequency rise from nearly the square of the refractive index, only shortly below the

(38) Clusius and Frank, *Z. physik. Chem.*, **34B**, 405 (1936).

melting point  $-38.2^{\circ}$ . Sufficiently high frequencies might convert the chloride and bromide curves to ones resembling the iodide.

Examination with the polarizing microscope revealed an apparently anisotropic lattice above the transition, which was replaced by one of much stronger birefringence below it. Suspected impurities make uncertain a definite assignment of non-cubic class to the high temperature form.

The melting behavior of *t*-butyl iodide is in agreement with the theory of melting point variation in isomeric and otherwise similar substances previously proposed.<sup>3</sup> Its gain of librational freedom postpones the melting point to  $234.9^{\circ}\text{K}$ .,  $65.3^{\circ}$  higher than *n*-butyl iodide, m. p.  $169.6^{\circ}\text{K}$ ., and  $55.3^{\circ}$  higher than *i*-butyl iodide, m. p.  $179.6^{\circ}\text{K}$ ., and  $65.8^{\circ}$  higher than *s*-butyl iodide, m. p.  $169.1^{\circ}\text{K}$ .

The present results show the variation in intermolecular action of nearly spherical molecules produced when atoms of gradually increasing size and polarizability are successively substituted as one of four groups about a central atom, the other three groups remaining unchanged. As noted previously,<sup>3,4</sup> the orientational interaction is found to be very sensitive to structure. A further method of studying the possible coupling is to dilute the dipoles in the solid state, preferably by solid solution formation with a similar, non-polar substance. A preliminary microscopic examination of a 50% by volume mixture of *t*-butyl chloride and carbon tetrachloride revealed that, as would be expected, the transition was made less sharp, and was displaced to lower temperatures, and that the whole solid formed an isotropic high temperature system, which would be anticipated from the known high temperature cubic form of carbon tetrachloride. However, partial melting was found to occur sharply and uniformly, leaving a skeleton-like isotropic lattice which itself melted sharply a few degrees higher. Dielectric measurements on such a system might show a complex behavior because of the coexistence of phases.

The discovery of rotational freedom in the solid forms of these simple molecules suggests

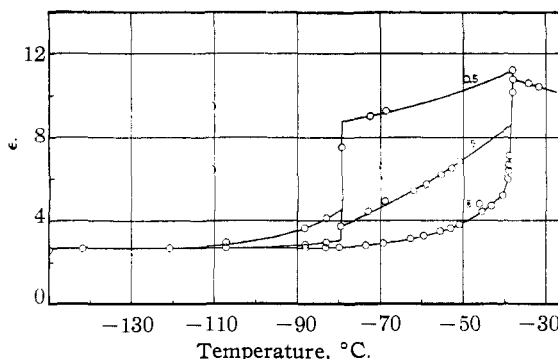


Fig. 7.—Temperature dependence of the dielectric constant of *t*-butyl iodide.

experiments to discover its effect on other physical properties. That is, the form of the solid above the transition might differ significantly from that below it in temperature coefficient of thermal conductivity, diffusion, solution rate and sublimation vapor pressure. If these processes were thus connected with rotation or non-rotation, information on their mechanism would be gained.

#### Summary

Polymorphism has been found and studied by means of thermal, optical and dielectric measurements in *t*-butyl chloride, bromide and iodide. Dispersion, hysteresis and supercooling effects have been interpreted in terms of possible molecular processes. Solid state transitions of the first kind are attended by supercooling when a relatively small free energy difference obtains between the metastable and the stable phases below the transition. The dielectric results indicate that this supercooling may be a function of the ordering ability of the molecules in the stable form. Rotational "premelting" before a solid state transition is analogous to the premelting found in solids near the melting point. Results with the polarizing microscope establish a correlation of lattice symmetry with molecular rotational freedom, and, conversely, the isotropic lattices previously found for many organic molecules above polymorphic transitions are associated with the development of rotational freedom at such transitions.