The Dielectric Behavior, Supercooling, and Vitrification of Certain Chlorobutanes and Chloropentanes

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Previous investigations by means of dielectric constant measurements, temperature–time cooling curves, and the polarizing microscope have shown that the molecules of the t-butyl halides[1] and the methyl chloromethanes,[2] like other molecules which do not depart too far from spherical symmetry, rotate in isotropic crystal lattices for some distance below the melting points. The disappearance of molecular rotation is normally accompanied by transition to an anisotropic lattice. At the other extreme of molecular shape, long-chain molecules, which are already more or less oriented relative to one another in the liquid state, crystallize rather readily to an anisotropic lattice without much tendency to supercool or vitrify.[3] The straight-chain paraffins[4] and alkyl halides[5] and cetyl alcohol[6] exemplify this behavior. The branched-chain molecules of i-propyl bromide, which are more unsymmetrical than t-butyl bromide because of the replacement of a methyl group in the latter by a hydrogen, showed about 11° of supercooling before crystallizing to an anisotropic lattice, in which no molecular rotation occurred.[5] The branching of the carbon chains in i-butyl and i-amyl bromides gave rise to glass-formation,[3] as did also the presence of similar branches in the chains of hydrocarbon molecules.[4] In considering these results, it should be borne in mind that a methyl group is not very different in size or shape from the atoms of chlorine and bromine, the van der Waals radius of the methyl group being 2.0 Å., that of the chlorine atom 1.80 Å., and that of the bromine atom 1.95 Å.[7] The present paper reports measurements made upon molecules into which dipoles are introduced by the replacement of methyl groups by chlorine atoms.

The dielectric constant measurements were made with a capacity bridge coupled to a variable oscillator in the fashion previously described,[1,8]

and the substances were further examined down to liquid air temperatures with a polarizing microscope[1] and by means of temperature–time curves.

Purification of Materials

i-Butyl Chloride.—Material from the Eastman Kodak Company was shaken with 10% potassium hydroxide solution, washed with water and dried over calcium chloride. Repeated fractionation in a 30-inch column gave a product boiling constantly at 68.2°; m. p. −130.3°; $n^{15}D$ 1.40047. The specific conductances at 13.9° were 3.0 × 10⁻¹⁰ at 50 kc., 0.5 × 10⁻¹⁰ at 5 kc., and 0.15 × 10⁻¹⁰ at 0.5 kc., so small as to prove the absence of any considerable amount of ionic impurity. Timmermans and Martin[9] give b. p. 68.85°, f. p. −131.2°, $n^{15}D$ 1.40096.

i-Amyl Chloride.—Material from the Eastman Kodak Company was treated with concentrated sulfuric acid, washed with water until the oil formed no immediate precipitate with alcoholic silver nitrate, dried over potassium carbonate and calcium chloride, and repeatedly fractionated in a 30-inch column; b. p. 98.1°; f. p. −104.4°; $n^{20}D$ 1.4087. Hass, McBee and Weber,[10] who have pointed out the unreliability of the values for the physical constants of the isomeric amyl chlorides in the literature, give b. p. 98.8°, while Timmermans[11] gives b. p. 99.15°. "International Critical Tables" gives $n^{20}D$ 1.4103.

t-Amyl Chloride.—Material from the Eastman Kodak Company was dried over calcium chloride and phosphorus pentoxide. Fractionation in a 30-inch column led to some decomposition as evidenced by olefin formation and evolution of hydrogen chloride. The compound was, therefore, dried over anhydrous carbonate and fractionated in a Vigreux column under reduced pressure, the middle fractions being retained. This procedure was repeated until a liquid of low specific conductance was obtained; $n^{20}D$ 1.40513; f. p. −73.7°; m. p. −73.3°. Literature values include: $n^{20}D$ 1.4053;[12] f. p. −72.7°.[11]

1,2-Dichloroisobutane.—"Practical" material from the Eastman Kodak Company was treated repeatedly with concentrated sulfuric acid, sodium carbonate solution, and water. A careful fractionation in a 30-inch column, drying with calcium chloride, and a second fractionation gave a product with b. p. 107.9°; $n^{20}D$ 1.43630. Literature values[13] are b. p. 106.5°; $n^{20}D$ 1.4370. The differences between these values and those for the sample obtained here, as well as the change of boiling point during the final distillation, indicated the presence of impurities in our sample. However, the low conductance of the liquid showed these impurities to be non-ionic. It is probable that they were other chlorinated hydrocarbons, present in small amounts.

(1) Baker and Smyth, THIS JOURNAL, **61**, 2798 (1939).

(2) Turkevich and Smyth, *ibid.*, **62**, 2468 (1940).

(3) Baker and Smyth, *ibid.*, **61**, 2063 (1939).

(4) Smittenberg, Hoog and Henkes, *ibid.*, **60**, 17 (1938).

(5) Baker and Smyth, *ibid.*, **61**, 1695 (1939).

(6) Baker and Smyth, *ibid.*, **60**, 1229 (1938).

(7) Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., p. 189.

(8) Smyth and Hitchcock, THIS JOURNAL, **54**, 4631 (1932); **55**, 1830 (1933).

(9) Timmermans and Martin. *J. Chim. Phys.*, **23**, 747 (1926).

(10) Hass, McBee and Weber, *Ind. Eng. Chem.*, **27**, 1190 (1935).

(11) Timmermans, *Bull. soc. chim. Belg.*, **30**, 62 (1921).

(12) Simons, Fleming, Whitmore and Bissinger, THIS JOURNAL, **60**, 2267 (1938).

(13) Hersh and Nelson. *ibid.*, **58**, 1631 (1936).

2,2-Dimethylbutane.—A sample was made available through the kindness of Dr. Mark Fred of the Ryerson Physical Laboratory, University of Chicago.

Experimental Results

The dielectric constants ϵ and the specific conductances were measured at frequencies of 50, 5, and 0.5 kilocycles. For i-amyl chloride, the specific conductances varied from the 23.6° values, 1.14×10^{-10} at 50 kc. and 0.137×10^{-10} at 0.5 kc. to the -128.4° values, 2.96×10^{-10} at 50 kc., 0.274×10^{-10} at 5 kc., and 0.092×10^{-10} at 0.5 kc., while, for t-amyl chloride, the conductances vary from the -50.4° values, 44.0×10^{-10} at 50 kc., 44.0×10^{-10} at 5 kc., and 43.3×10^{-10} at 0.5 kc., down to the -189.0° values, about 0.1×10^{-10} at 5 kc., and 0.4×10^{-10} at 0.5 kc. As the amounts of anomalous dispersion shown by both the conductance and the dielectric constant values for i-amyl and t-amyl chloride are too small to be significant, the dielectric constants are shown only at 50 kc. for these substances in Table I, the values at 5 and 0.5 kc. being practically the same as these, while the specific conductances are omitted entirely. For i-butyl

TABLE I

(CH₃)₂CH(CH₂)₂Cl

t, °C.	ϵ(50 kc.)	t, °C.	ϵ(50 kc.)	t, °C.	ϵ(50 kc.)
Cooling		−121.4	11.26	−106.0	4.03
23.6	5.97	−127.2	11.64	−105.5	4.54
18.8	6.10	−129.9	11.84	−105.1	5.18
6.9	6.35	−130.3	11.91	−104.9	5.63
− 0.9	6.50	−115.3	2.99	−104.8	5.86
− 29.5	7.25	−128.4	2.84	−104.6	6.63
− 40.7	7.61	Heating		−104.4	7.58
− 50.3	7.89	−114.2	2.95	−104.3	8.00
− 66.6	8.51	−111.6	3.03	−104.0	10.15
− 77.7	8.93	−109.2	3.20	−103.7	10.14
− 94.0	9.72	−108.1	3.35	−100.0	9.98
−102.4	10.13	−106.8	3.67	− 93.4	9.65
−108.8	10.51	−106.6	3.75	− 24.7	7.12

CH₃CH₂CCl(CH₃)₂

t, °C.	ϵ	t, °C.	ϵ	t, °C.	ϵ
Cooling		−74.9	3.47	−73.8	3.08
−50.4	12.31	−77.8	2.81	−73.7	3.34
−58.8	13.05	−129.3	2.36	−73.6	3.49
−66.2	13.77	−143.9	2.32	−73.5	3.90
−71.9	14.38	−170.6	2.28	−73.4	4.42
−77.4	14.99	−189.0	2.27	−73.3	5.85
−79.7	15.30	Heating		−73.3	7.27
−74.0	13.03	−137.5	2.32	−73.2	9.76
−73.7	12.87	−109.3	2.36	−73.2	12.41
−73.7	12.64	−97.8	2.39	−73.1	14.10
−73.7	9.55	−82.3	2.40	−72.7	14.34
−73.8	5.43	−78.5	2.42	−72.3	14.38
−74.2	4.13	−74.2	2.46	−65.7	13.72

(CH₃)₂CHCH₂Cl

t, °C. Kc	50	5	Cooling 0.5	50	5	0.5
		ϵ			ϵ''	
13.9	6.49	6.54	6.63	0.011	0.018	0.054
−38.2	7.87	7.80	8.00			
−89.3	10.10	10.07	10.08			
−108.5	11.29	11.29	11.28	.013	.011	.018
−120.2	12.15	12.14	12.14	.004	.004	.018
−138.2	13.73	13.71	13.66	.007	.004	.018
−147.7	14.66	14.67	14.63	.031	.005	.018
−155.6	15.50	15.52	15.45	.193	.035	
−159.2	15.73			1.06		
−160.0		15.89				.165
−161.2	15.25			2.54		
−161.7	14.84			3.07		
−162.3		16.04				.330
−162.6			16.00			.14
−163.2		16.09				.80
−164.0	10.67			4.3		
−164.7		15.89				1.78
−164.9			16.19			.66
−165.3	7.73			4.25		
−165.6		15.24				2.94
−165.7			16.30			1.04
−165.9	6.71			3.74		
−166.1		14.37				3.81
−166.4			16.47			1.89
−167.0	5.40			2.70		
−167.7	4.64	10.55		1.98	4.99	
−168.0			15.56			5.03
−168.6		8.00			4.25	
−169.2			13.25			8.06
−169.8	3.63			0.99		
−170.3		5.39			2.52	
−170.6			8.76			7.54
−170.9		4.89			2.00	
−171.1			7.53			6.81
−171.4	3.27			.56		
−171.6		4.28			1.45	
−171.8			6.02			5.20
−172.2			5.50			4.48
−173.4	2.94			.28		
−174.0		3.34			.53	
−174.6			3.67			1.49
−185.9		2.41			.029	
−189.7	2.35	2.37	2.38	.02	.024	.02
−188.8	2.38	2.39	2.38	.002		.02
−182.6	2.43	2.42	2.39	.014	.02	.11
−180.8	2.43	2.48	2.52	.025	.047	.14
−179.1	2.47	2.56	2.62	.043	.074	.24
−176.8	2.56	2.74	2.91	.068	.162	.52
−174.7	2.70	3.02	3.44	.157	.352	1.33
−173.8			3.80			1.85
−172.7	2.98	3.60	4.61	.298	.78	3.17
−171.1		4.35			1.45	
−170.8			6.91			5.96
−169.7	3.64			.819		
−169.5		5.63			2.61	
−169.2			10.86			7.59
−168.5		6.96			3.48	
−168.2			13.04			5.9
−167.7	4.27			1.46		

TABLE I (Concluded)

Kc, t, °C.	ε, 50	ε, 5	ε, 0.5	ε'', 50	ε'', 5	ε'', 0.5
−167.5		8.92			4.00	
−167.1			13.76			3.2
−166.7	4.90			2.13		
−166.4		10.89			3.58	
−166.1			13.34			1.6
−165.6	5.77			2.71		
−165.3		11.76			2.30	
−164.5	6.81			3.02		
−164.2		11.41			1.31	
−163.9			11.20			0.32
−163.3	7.94			2.72		
−162.8		10.07			0.44	
−162.5			9.50			.14
−161.8	8.05			1.47		
−161.4		8.23			.13	
−161.0			7.64			.07
−159.7	6.21			0.37		
−158.9		5.42			.024	
−158.4			4.82			.05
−157.1	3.59			.033		
−156.3			2.93			.04
−155.9	2.45			.002		
−156.9	2.34	2.33	2.31			.04
−146.6	2.24	2.25	2.22			.02
−133.9	2.43	2.46	2.44			.02
−132.1	2.78	2.78	2.76			
−131.3	3.31	3.36	3.36			
−130.8	4.30	4.37	4.38			
−130.7	4.88	4.99	5.01			
−130.4	6.78	6.99	7.12			
−130.3	8.42	8.62	8.71			
−130.2	9.48	9.89	10.00			
−130.2	10.88	11.24	11.40			
−130.0			12.76			
−129.6	12.95					
−128.9			12.81			
−126.4	12.68	12.64	12.58			
−120.4	12.21	12.23	12.31			
−87.4	10.04	10.01	10.01			

(CH₃)₂CHClCH₂Cl

Kc, t, °C.	ε, 50	ε, 5	ε, Cooling 0.5	ε'', 50	ε'', 5	ε'', 0.5
22.8	7.15	7.14	7.13	0.057	0.416	4.06
−3.0	8.01	8.02	8.00	.050	.300	2.86
−23.2	8.83	8.87	8.88	.031	.154	1.36
−34.1	9.34	9.37	9.37	.030	.127	1.07
−42.5	9.80	9.81	9.79	.028	.105	0.91
−63.1	10.97	10.97	10.95	.023	.11	.87
−66.1	11.29	11.29	11.23	.017	.042	.34
−92.2	13.32			.024		
−99.0	13.88	13.89	13.86	.019	.041	.26
−108.0	14.87	14.87	14.85	.019	.056	.36
−113.4	15.51			.042		
−122.5	16.74	16.70	16.70	.104		.21
−126.7	17.37	17.32	17.36	.292		.17
−128.9	17.64			.497		
−131.5	17.93	18.05	18.08	1.09	.44	.33
−132.9	17.94			1.79		
−134.1	17.68	18.38		2.72	.62	
−135.5	16.67	18.71	18.79	3.9	**1.19**	**0.52**
−136.5	15.29			4.97		
−137.3	13.79			5.42		
−138.2		19.75				**1.98**
−138.5	11.45			5.44		
−139.1		18.60			2.54	
−139.6	9.37			4.90		
−139.8		18.03			4.1	
−140.0		17.81			5.03	
−140.1			19.79			2.52
−140.8	7.66			4.05		
−141.2	7.08			3.67		
−141.7		13.96			6.0	
−142.3		20.24				2.73
−143.0		18.17				7.16
−143.5		9.70			5.4	
−144.2		8.97	14.63		4.64	10.2
−144.4	4.65			1.69		
−145.3		12.00				9.90
−145.5	4.12			1.22		
−146.3		9.48				8.46
−146.4		5.54			2.78	
−146.9		7.84				7.63
−147.6		4.71			1.37	
−147.9	3.39	4.63	6.54	.60	1.44	5.62
−154.5		3.21				1.48
−155.1	2.66			.148		
−155.6		3.03				0.90
−156.4		2.75			0.164	
−157.3	2.51			.082		
−164.0		2.54				.014
−165.0	2.43			.085		
−180.6		2.39				.29
−187.8	2.36	2.36	2.36		.008	.076

chloride and 1,2-dichloroisobutane, the values of the dielectric constant are given at all three frequencies, as are the values of the imaginary part of the dielectric constant ϵ'' calculated from the specific conductance k in reciprocal ohms and the frequency f in kilocycles by means of the equation $\epsilon'' = 1.8 \times 10^9\, k/f$. The values of k are omitted from Table I since they are obtainable by application of this equation to the values of ϵ''. The data are plotted against temperature in the accompanying diagrams. For the sake of brevity, many experimental values which would lie accurately on these curves are omitted both from the curves and from Table I. As the numerous heating and cooling curves for 1,2-dichloroisobutane agreed closely with one another with the exception of the dotted line in Fig. 5 obtained after special heat treatment, the data for this substance are taken indiscriminately from cooling and heating runs. Occasional discrepancies among small ϵ'' values are due to the relatively large experimental errors in these values, which are too small to be of significance.

Discussion of Results

Attempts to get the *i*-amyl chloride as a glass in a region of temperature where anomalous dispersion could be observed were unsuccessful. A glass was obtained by plunging the cell containing the liquid directly into liquid air, but, on subsequent warming, crystallization occurred with such rapidity that the cell was shattered. Cooling at rates varying from 0.15° per minute to 5.1° per minute invariably resulted in the commencement of crystallizaton at about −129°, that is, after about 26° of supercooling. As the heat of crystallization of the substance was insufficient to raise its temperature up to the true freezing point, the trend of the dielectric constant during solidification is represented by the dotted line in Fig. 1. It fell to the low value arising from
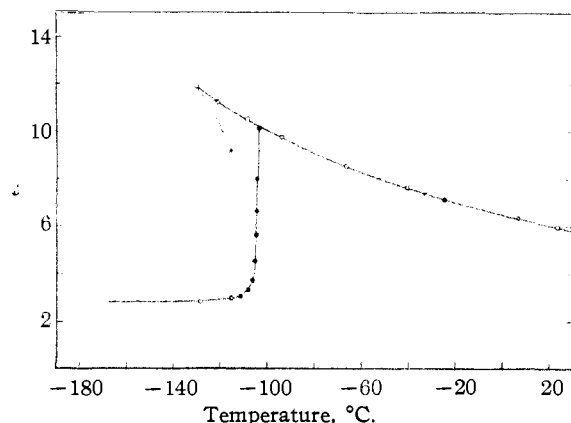
Fig. 1.—Temperature dependence of the dielectric constant of *i*-amyl chloride (hollow circles represent points on cooling curve, filled circles, points on heating curve).

electronic and atomic polarizations, freedom of molecular rotation being absent. On heating, the low value of the dielectric constant prevailed until about 5° below the melting point when the gradual rise commonly observed just below the melting point set in. At the melting point, −104.6°, the dielectric constant rose sharply to the value found for the liquid on cooling. No anomalous dispersion of the dielectric constant larger than the experimental error was evident, although the beginning of such an effect was evidenced in the region of supercooling by increase with falling temperature in the small values of ϵ'' at 50 kc., from 0.005 at −102.4° to 0.027 at −129.9° and in the values of ϵ'' at 5 kc., from 0.0057 at −108.8° to 0.011 at −130.1°. The failure of *i*-amyl chloride to vitrify under normal

conditions is in contrast with the behavior of the bromide and of *i*-butyl chloride and bromide.
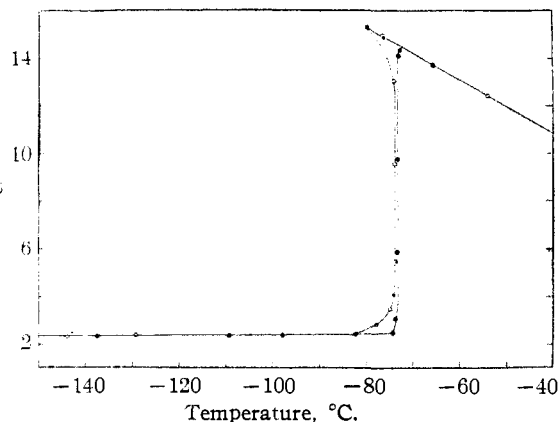
Fig. 2.—Temperature dependence of the dielectric constant of *t*-amyl chloride (hollow circles represent points on cooling curve, filled circles, points on heating curve).

Figure 2 for *t*-amyl chloride shows the normal increase in dielectric constant with decreasing temperature of the liquid down to −80°, where the liquid crystallized after about 6° of supercooling. The dielectric constant dropped sharply to a low value of about 2.3, where it remained down to −190°. No solid transition could be detected either thermally or dielectrically below the freezing point. The rounding off of the ϵ value near the end of freezing presumably represents a lack of thermal equilibrium. The heating curve shows essentially the same behavior. The low value of the dielectric constant for the crystalline solid rose very sharply at the melting point to the value for the liquid. A slight dispersion, at most 0.2 unit difference between 50 and 0.5 kc., found just below the melting point does not necessarily mean a loosening of the lattice ("premelting"), but probably is the effect of a trace of an ionic impurity which caused much greater dispersion in less pure samples. The low value of ϵ for 50 kc. right up to the melting point is evidence for lack of premelting in this case. Investigation with the polarizing microscope showed that the sample crystallized in an anisotropic system. A slight amount of hysteresis in the melting and freezing points was observed. On cooling, the well-defined flat on the time–temperature curve, as well as the sharp drop in the dielectric constant, occurred at −73.7°. On heating, the mid-point in the rise in dielectric constant was at −73.3°. Such hysteresis effects have been found previously[5] to be associated with monotropic transi-

tions near the melting point. The difference here reported is very small and no evidence for a solid transition in the case of t-amyl chloride could be found either thermally, dielectrically or optically. The dielectric constant of the solid is constant and close to the square of the refractive index right up to the melting point. The only rotational motion which the dielectric studies would not detect is that around the axis of the carbon–chlorine bond. Because of the shape of the molecule, such motion is extremely improbable.

The dependence of the dielectric constant of i-butyl chloride upon falling temperature established by numerous runs is shown in the upper half of Fig. 3. The liquid does not crystallize on cooling, but vitrifies at some distance below the freezing point, the cooling curves closely resembling those previously found[3] for i-butyl bromide and i-amyl bromide. The glass behaves like a very viscous liquid. The relaxation time of the molecules increases with falling temperature and increasing viscosity of the material until
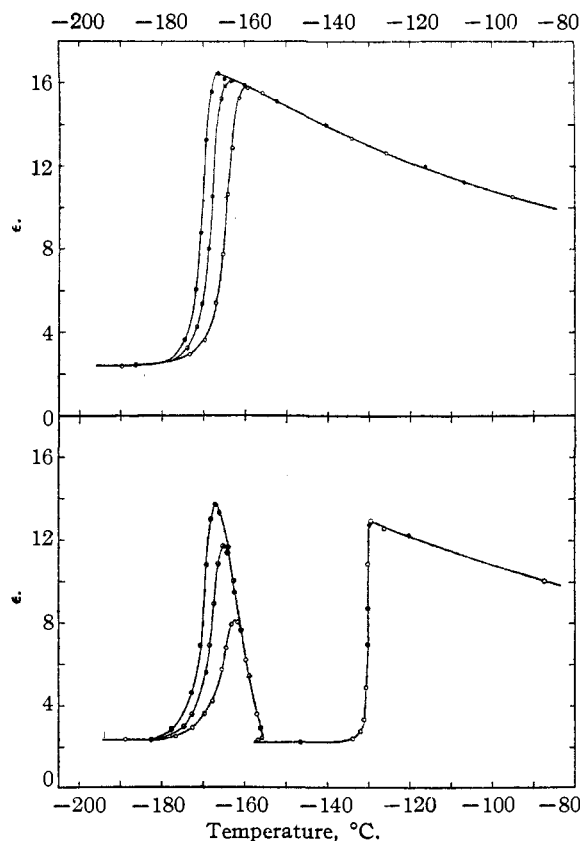
Fig. 3.—Temperature dependence of the dielectric constant of i-butyl chloride (upper curves, cooling; lower curves, heating after 27 hrs. at −185°; hollow circles, at 50 kc.; half-filled circles, at 5 kc.; filled circles, at 0.5 kc.).

the orientation of the molecules lags behind the alternating electric field used in the measurement. The consequent anomalous dispersion of the dielectric constant causes the dielectric constant–temperature curve to separate into branches which unite again when the molecules are entirely unable to orient in the field even of the 0.5 kilocycle current. In this region of anomalous dispersion, the imaginary part of the dielectric constant goes through a maximum as shown in Fig. 4.
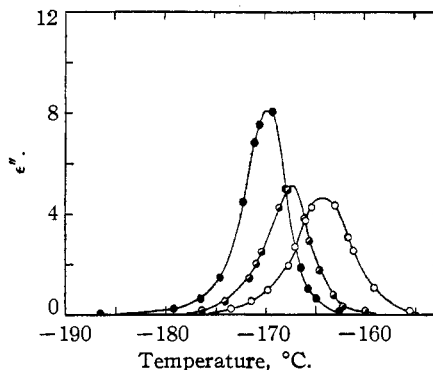
Fig. 4.—Temperature dependence of ϵ'' for i-butyl chloride (hollow circles, at 50 kc.; half-filled circles, at 5 kc.; filled circles, at 0.5 kc.).

The behavior of the glass on warming provides confirmation of the explanation offered[3] for the behavior of the i-butyl and i-amyl bromide glasses on warming. The dielectric constant-temperature curves in the lower half of Fig. 3 were obtained on warming a specimen of the i-butyl chloride glass which had been kept between −180° and −190° for twenty-seven hours. Another run, after the glass had been kept at this low temperature for twenty-five hours, duplicated this behavior exactly. After the glass had been kept at this low temperature for 100 hours, the behavior was very similar, crystallization becoming apparent at about the same temperature, −170°, but occurring at a noticeably faster rate. The dielectric constant curves obtained on warming the glass up from −185° are identical with the cooling curves up to about −168°, above which the dielectric constant values begin to fall below those obtained at the same temperatures on cooling. This change in the curves is due to crystallization of the glass, which proceeds faster and faster. The sample heats up above the temperature of the thermostat, and the dielectric constant goes through a maximum and then drops to a low value characteristic of a crystalline solid having molecules unable to rotate. A small drop in

temperature occurs after crystallization has been completed when the sample cools down to the thermostat temperature. Further heating reveals no great change in the dielectric properties until around −135°, when, after a little premelting rise in the dielectric constant, the sample melts at −130.5°, and the dielectric constant rises sharply to the values characteristic of the liquid at that temperature. The crystallization of the glass on warming could be observed visually and also under the polarizing microscope, the isotropic glass changing to anisotropic crystals which melt sharply.

The extremely critical nature of the crystallization processes in a glass are exemplified by some preliminary rate studies. The procedure followed was to cool the sample at the same rate for each run to the desired temperature. This was then kept constant by manual additions of liquid air. The constancy of temperature was such that the platinum resistance thermometer at the center of the sample showed variations of less than ±0.3° over periods of several hours. More than two hours at −146.5° or higher resulted in no sign of crystallization as evidenced by no change in dielectric properties. Likewise, cooling down to −169.6°, and keeping there for periods of three hours resulted in no lowering of the dielectric con-

stant or of the specific conductance. However, warming up a few degrees from this temperature resulted in crystallization.

Apparently the practical regions of crystallization are between around −168 to −148°. Two runs were made during which the temperature was kept constant during the crystallization process in this region. The rate of crystallization was estimated from the decrease in conductivity at 50 kc. The assumption was made that the observed conductivity was the sum of the conductivity of the crystal (here, practically, zero) and the conductivity of the glass. Curves obtained by plotting the total decrease in specific conductance against time proved to be straight lines for most of the course of crystallization. The rate of crystallization as determined by the slopes of the lines was less at −149° than it was at −155.5°.

The dielectric constant–temperature curves for 1,2-dichloroisobutane are shown in Fig. 5. On cooling, the substance vitrified to a clear glass with a resulting dielectric behavior similar to that found in the case of other organic glasses. The mechanical vitrifying point, at which the thermometer could still be turned in the cell, could not be determined accurately, but was definitely below −130°, at which temperature dispersion of the 50 kc. dielectric constant began. Subsequent investigations by Dr. W. P. Conner showed that the material was very viscous at −151° and mechanically rigid at −166°. The rates of cooling down to liquid air temperatures were varied somewhat, but, except for cases where lack of thermal equilibrium was obviously present, were without effect on the dielectric constant-temperature curve. Most of the cooling runs were made at an average rate of 0.15° per minute below −100°. Heating curves on the glass reproduced exactly the dielectric constant–temperature curve found on cooling except for the cases of special heat treatment mentioned below. 1,2-Dichloroisobutane thus behaves in marked contrast to the relatively unstable halogenated hydrocarbon glasses previously studied dielectrically. It bears much more resemblance to the stable glasses formed by some organic substances containing hydroxyl groups.[14] We were never able to produce complete or even extensive crystallization in 1,2-dichloroisobutane and thus could not establish its melting point with certainty. This
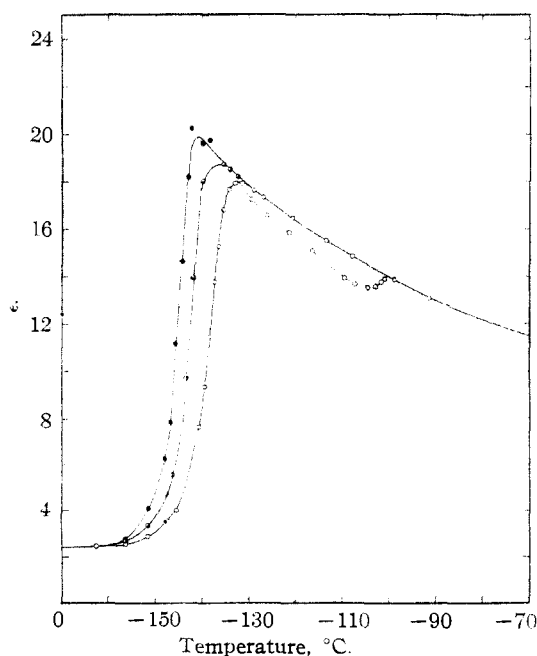

Fig. 5.—Temperature dependence of the dielectric constant of 1,2-dichloroisobutane (hollow circles at 50 kc.; half-filled circles at 5 kc.; filled circles at 0.5 kc.; dotted curve, heating after 30 hrs. at −185° and 6 hrs. at −132°).

(14) Tammann, "Der Glaszustand," Verlag L. Voss, Leipzig, 1933.

physical constant is also absent from the results of other investigators. Similarly, the polarizing microscope failed to reveal any signs of anisotropy, which would give evidence of crystal formation.

Several rather drastic attempts were made to crystallize the 1,2-dichloroisobutane. Cooling down to $-132.5°$, the point at which dispersion of the 50 kc. dielectric constant sets in, and holding the sample within 1° of this temperature for six hours did not change the dielectric constant or its behavior on heating. However, cooling the sample down to liquid air temperatures, keeping it there for thirty hours, warming it up to $-132.5°$ during the course of sixteen hours, and holding it there for six hours caused the dielectric constant to drop from 17.90 to 17.62. Further very slow warming caused the dielectric constant to follow a curve about 1.20 units below the normal one at $-110°$, as represented by the dotted line in Fig. 5, the data for which are omitted from Table I. At around $-105°$, this dielectric constant–temperature curve turned upward again, so that, from $-100°$ up, the values were identical with the normal cooling and heating runs. This behavior on annealing, following cooling to liquid air temperatures, may be interpreted as a partial crystallization of the sample, which would place the melting point of 1,2-dichloroisobutane at about $-100°$. In subsequent work by Dr. W. P. Conner upon the same sample of 1,2-dichloroisobutane, the material was cooled to $-166°$, raised slowly to a temperature above the approximate melting point, cooled to $-162°$, warmed to $-142°$ and kept within about 4° of this temperature for forty-eight hours. Although this location on the dielectric constant–temperature curve is analogous to that at which crystallization set in on the corresponding curve for i-butyl chloride, no dielectric constant change indicative of crystallization was brought about by this heat treatment.

Figure 6 shows the imaginary part of the dielectric constant at three frequencies plotted against temperature for 1,2-dichloroisobutane. The curves are similar to those obtained with falling temperature for the i-butyl chloride glass in Fig. 4. The maximum value of ϵ'' should be given approximately[15,3] by the relation $\epsilon''_{max.} = (\epsilon_1 - \epsilon_0)/2$ in which $\epsilon_1 =$ dielectric constant at zero frequency, and $\epsilon_0 =$ dielectric constant at infinite frequency. It is interesting to compare
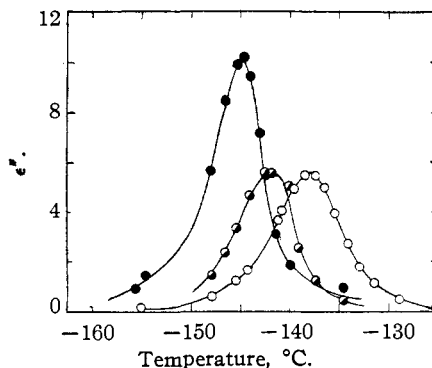
(15) Yager, *Physics*, **7**, 434 (1936).

Fig. 6.—Temperature dependence of ϵ'' for 1,2-dichloroisobutane (hollow circles at 50 kc.; half-filled circles, at 5 kc.; filled circles, at 0.5 kc.).

the values of $\epsilon''_{max.}$ of the curves in Figs. 4 and 6 with those calculated from the above relation. ϵ_1 may be obtained by extrapolating the values of ϵ above the dispersion regions in Figs. 3 and 5 to the temperatures at which $\epsilon''_{max.}$ is found in Figs. 4 and 6. The values of ϵ_0 are given by the values of ϵ for the solids at the lowest temperatures. The results are tabulated in Table II at each frequency, f.

TABLE II

CALCULATED AND OBSERVED VALUES OF $\epsilon''_{max.}$

	f, kc.	$\epsilon''_{max.}$ Calcd.	Obsd.
i-Butyl chloride	50	7.0	5.2
	5	7.3	5.4
	0.5	7.4	8.3
1,2-Dichloroisobutane	50	8.5	5.5
	5	9.0	5.8
	0.5	9.5	10.5

The observed and the calculated values in Table II are of the same order of magnitude, but it is only the 0.5 kc. values which show approximate agreement. The maxima for the 5 and the 50 kc. curves are lower and broader in proportion to their height, which suggests greater inhomogeneity of particle size in the glasses at these temperatures, since such inhomogeneity would lower the values of $\epsilon''_{max.}$ and broaden the curves.[16]

2,2-Dimethylbutane, on examination under the polarizing microscope, was found to freeze to an isotropic solid. At much lower temperatures, it underwent an enantiotropic transition to an anisotropic form. The peculiar behavior in the immediate vicinity of the freezing point noted by Hicks-Bruun, Bruun and Faulconer,[16] could not be detected by the methods used here. The

(16) Hicks-Bruun, Bruun and Faulconer, THIS JOURNAL, **61**, 3099 (1939).

transition is evidently the one previously reported[17] at $-146.1°$, which involves an entropy change of 8.61 units as compared to an entropy of fusion of 0.64 unit.[17] The hydrocarbon t-butylethylene similarly has a solid transition at $-148.2°$ with an entropy change of 8.32 units, while it melts at $-114.7°$ with an entropy of fusion of 1.65 units.[18] These data, together with our polarizing microscope results on 2,2-dimethylbutane, point to rotational freedom in the solid state of both hydrocarbons between the transition and melting points.

t-Amyl chloride can be considered as derived from 2,2-dimethylbutane by the substitution of a chlorine atom for a methyl group. Substitution of halogen for methyl groups in neopentane,[1,2] hexamethylethane[19] and hexamethylbenzene[20] has not eliminated rotational freedom in the solid forms. The dielectric and thermal studies here reported, however, indicate no such freedom in solid t-amyl chloride. 1,2-Dichloroisobutane also is sterically very similar to both 2,2-dimethylbutane and t-amyl chloride. However, here the replacement of a methyl group in t-amyl chloride by a chlorine atom leads to an unusual tendency toward glass formation. As previously pointed out, annealing runs indicate the probability of a melting point at about $-100°$ for 1,2-dichloroisobutane. 2,2-Dichloropropane, which possesses freedom of molecular rotation in the solid, melts at $-34.4°$, while 1,3-dichloropropane, whose molecules do not rotate in the solid, melts at $-99.4°$. This low melting point, which is characteristic of an absence of molecular rotation,[5] as well as the drop of the dielectric constant on partial crystallization, indicates that, in the crystalline state, the molecules of 1,2-dichloroisobutane do not rotate.

The difference in behavior between these three sterically similar compounds may be ascribed to the differences in force fields and in symmetry. The introduction of good-sized dipoles and the decrease of symmetry caused by the presence of chlorine atoms are apparently enough to prevent rotation in the solid state. This is surprising, however, in view of the lack of such effects when methyl groups in neopentane, hexamethylethane,[19] and hexamethylbenzene[20] are replaced by chlorine atoms.

(17) Stull, THIS JOURNAL, **59**, 2726 (1937).
(18) Kennedy, Shomate and Parks, *ibid.*, **60**, 1507 (1938).
(19) White and Bishop, *ibid.*, **62**, 8 (1940).
(20) White, Biggs and Morgan, *ibid.*, **62**, 16 (1940).

An important factor to be considered in connection with the supercooling or vitrification of these substances is the strong probability that their molecules exist in the liquid in several different internal configurations arising from rotation around the bonds into positions of minimum potential energy separated from one another by fairly high potential barriers. In a crystal made up of non-rotating molecules it is very probable that, of all the possible internal configurations of the molecule, only those of a certain form are allowed. In 2,2-dimethylbutane all three possible internal configurations are mutually superimposable, but this is not the case in t-amyl chloride or 1,2-dichloroisobutane. Since molecules with all the internal configurations are, presumably, present in the liquid, it may be that lag in conversion into the configuration necessary to fit into the crystal is responsible for the tendency of the t-amyl chloride to supercool and the great reluctance of the 1,2-dichloroisobutane to crystallize.

The dependence upon molecular shape of the tendency of a liquid to crystallize, to supercool, or to vitrify has been discussed previously in some detail.[3] General observations must be of a somewhat approximate nature because of the influence upon the behavior of the substance of previous history and purity of the material, thermal treatment, and general experimental conditions. It is of interest to compare the behavior of the chlorides discussed here with that of similarly shaped bromides and hydrocarbons. In a tabulation of crystallization data of hydrocarbons by Smittenberg, Hoog and Henkes,[4] seven out of twenty-three pentanes, hexanes, heptanes, and octanes form glasses, all seven having branched chains. The straight-chain molecules crystallize, as do n-amyl bromide and the other straight-chain alkyl bromides. 2-Methylbutane is reported as crystallizing, while the similarly shaped molecules of i-butyl chloride and bromide formed glasses which crystallized only after prolonged cooling and thermal treatment. 2-Methylpentane is reported as forming a glass, as did the similarly shaped i-amyl bromide, while i-amyl chloride with the slightly smaller halogen on the end supercooled $26°$, but did not actually vitrify. Lengthening of the chain of the molecules with the single branch at the end as in 2-methylhexane seems to eliminate or reduce their tendency to vitrify. Of the five heptanes and octanes

which were found to vitrify, each possessed an asymmetric carbon atom, and only those five possessed an asymmetric carbon, which suggests that their vitrification may have been due to the presence of optical isomers. The cause of vitrification here would thus be analogous to the reason proposed for the vitrification of 1,2-dichloroisobutane, that is, the coexistence of different molecular forms. The vitrification or crystallization of the substances discussed in this paper is consistent with the guiding principles and tendencies previously discussed, but it is evident that a small difference in the size or the field of an atom or group in the molecule may greatly alter the tendency to vitrify.

Summary

The dielectric constants and specific conductances of i-butyl chloride, i-amyl chloride, t-amyl chloride, and 1,2-dichloroisobutane have been measured over a wide range of temperature at frequencies of 0.5, 5 and 50 kilocycles. The substances have also been observed over a wide range of temperature with a polarizing microscope.

The molecules of all four substances are too unsymmetrical to rotate in the crystalline state. t-Amyl chloride shows pronounced supercooling and i-amyl chloride very great supercooling. i-Butyl chloride vitrifies, but crystallizes at an intermediate temperature after long standing at liquid air temperature. 1,2-Dichloroisobutane vitrifies and shows only slight crystallization after prolonged thermal treatment.

The solid transition of 2,2-dimethylbutane has been found, by means of the polarizing microscope, to be enantiotropic, the high temperature form being isotropic and the low anisotropic. This, together with the high entropy of transition and low entropy of fusion, points to molecular rotation in the isotropic form.

The tendencies of these substances to crystallize or vitrify are compared with those of other alkyl halides and hydrocarbons. Some irregularity of molecular form and the possible coexistence of two or more molecular shapes contribute toward a tendency to vitrification. A small difference in the size of an atom or group in a molecule may make a large difference in the tendency to vitrify.

The Effect of Alkali Promoter Concentration on the Decomposition of Ammonia Over Doubly Promoted Iron Catalysts*

BY KATHARINE S. LOVE AND STEPHEN BRUNAUER

One of the many interesting unsolved problems of catalysis is the nature of the action of the alkali promoter in a doubly promoted iron synthetic ammonia catalyst. There is no doubt about the fact that the aluminum oxide promoter helps to create and maintain a large surface, since the total surface of singly promoted catalyst 954 (containing 10.2% aluminum oxide) is at least six times as large as that of a carefully reduced sample of pure iron catalyst 973. After continued operation at 450° the difference in surface becomes twentyfold.[1] However, the potassium oxide promoter showed no such surface enlarging action. It was pointed out by Emmett and Brunauer[2] that the total surface of catalyst 954 is about three times as large as that of doubly promoted catalyst 931

(containing 1.3% aluminum oxide and 1.6% potassium oxide), and yet the doubly promoted catalyst has a considerably greater activity toward the synthesis of ammonia at high pressures than the singly promoted catalyst. If one determines the number of iron atoms on the surface of these catalysts by chemisorption experiments[1,2,3] one finds that catalyst 954 has almost five times as many iron atoms on the surface as catalyst 931. It seems, therefore, that the alkali on the surface has some specific activating action on the neighboring iron atoms.

The kinetics of ammonia decomposition over catalyst 931 was calculated by Brunauer, Love and Keenan[4] from adsorption data. In their treatment of the problem the tacit assumption was made that every iron atom that is capable of chem-

* Not copyrighted.

(1) Emmett and Brunauer, THIS JOURNAL, **59**, 1553 (1937).

(2) Emmett and Brunauer, ibid., **59**, 310 (1937).

(3) Brunauer and Emmett, ibid., **62**, 1732 (1940).

(4) Brunauer, Love and Keenan, ibid., to be published.