lated the approximate number and constant for the three most active classes. We have been unable to determine the nature of these sites beyond the indication that some at least are associated with some of the anomalous carboxyl groups.

CAMBRIDGE 39, MASS.

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Molecular Shape and Rotational Freedom in the Tetrahalogenated Methanes in the Solid State[1]

BY ROBERT C. MILLER[2] AND CHARLES P. SMYTH

RECEIVED JULY 9, 1956

The dielectric constants of ten unsymmetrical tetrahalogenated methanes have been measured in the liquid and solid states at a frequency of 5 kc. over wide temperature ranges extending, in some cases, down to −196°. The freezing points and transition points shown by the dielectric constant–temperature curves are tabulated together with those given in the literature for the four symmetrical tetrahalogenated methanes. When the van der Waals radii along the carbon–halogen axes from the carbon nucleus differ by no more than 9%, molecular rotational freedom is observed in the solid in the temperature region between the freezing point and a rotational transition point. The effect upon the apparent dielectric constant value of shrinkage of the solid between the condenser plates with falling temperature is treated approximately. Specific volume is measured as a function of temperature for dibromodichloromethane and bromotrichloromethane, which have very small dipole moments, and used to calculate approximately the true dielectric constant–temperature curves. For substances in which the orientation polarization is small in comparison with the total polarization, these corrected curves are very different in shape from the uncorrected. The curves for several particularly pure substances indicate the existence of some molecular mobility for several degrees below the freezing point, confirming conclusions based on previous measurements.

Among many more or less symmetrical molecules which have been investigated for possible hindered rotation or order–disorder orientation in the solid state, methane,[3] deuteromethane[3] and the tetrasubstituted methanes[3] have seemed to offer an exceptionally good opportunity for controlled variation in the factors affecting molecular behavior. The critical wave lengths or dielectric relaxation times of a considerable number of tetrasubstituted methanes containing methyl and chloro, bromo, iodo or nitro groups in the pure liquid state or in solution have been measured.[4,5] Six tetrahalogenated methanes have been similarly investigated in the pure liquid state.[6] The present paper reports low frequency dielectric constant measurements upon these six substances in the solid state and similar measurements upon four other tetrahalogenated methanes. It also lists similar rotational transition points for the four symmetrical tetrahalogenated methanes,[7] whose non-polarity makes them less significant for dielectric measurements.

Purification and Properties of Materials

The authors wish to express their gratitude to E. I. du Pont de Nemours and Company for the gift of three of the substances in very pure form and to the Dow Chemical Company for successive samples of the difficultly obtainable tribromochloromethane. The other compounds were procured from Matheson, Coleman and Bell, Inc., and from Halogen Chemicals, Inc., as indicated in Table I. The sharpness of the freezing points on the dielectric constant–temperature curves shows high purity for all except, possibly, the tribromofluoromethane sample. The sources, freezing points and boiling points of the samples are listed in Table I.

TABLE I

SOURCE, PURIFICATION, MELTING POINT AND BOILING POINT OF COMPOUNDS

Compound	Source	M.p., °C. Obsd.	M.p., °C. Lit.	B.p., °C. Obsd.	B.p., °C. Lit.
CF_3Cl[a]	Matheson	−189.0	−181	−81.9	−80
CF_2Cl_2[a]	Matheson	−158.2	−160	−24.9	−28
CCl_3F[b]	Matheson	−109.5	−111	+24.4	24.1
CF_3Br[a]	du Pont	−175.5		−57.2	
CF_2Br_2[a]	du Pont	−110.1		+23.9	
CBr_3F[b]	Halogen	−74.5		+106	
CCl_3Br[c]	Matheson	−5.8	(−21)	103	104.1
CCl_2Br_2[d]	Matheson	+21.8	22	.....	
CBr_3Cl[d]	Dow	+55	55	.....	
CF_2BrCl[a]	du Pont	−159.5		−3.3	

[a] Distilled from cylinder directly into cell. [b] Fractionally distilled. [c] Dried over barium oxide, distilled and fractionally crystallized at the freezing point. [d] Washed with sodium thiosulfate, dried with barium oxide and fractionally crystallized at the freezing point.

Experimental Methods and Results

The dielectric constants ϵ' were measured at a frequency of 5 kilocycles over a wide range of temperature by means of the cell and impedance bridge previously described.[8,9] The dielectric losses at this frequency were negligibly small. The experimental results are shown in the accompanying graphs of dielectric constant plotted against temperature. The actual experimental points are so numerous and lie so well on the curves that they are omitted from the diagrams.

The dipole moments[6] of these molecules are so small that the orientation polarization due to the dipoles may, in some cases, be of the same order of magnitude as the changes of polarization accompanying density changes arising from phase transitions or from considerable changes in temperature. The effect of these density changes has been explored by measuring the densities of dibromodichloromethane and tribromochloromethane over a range of temperature from the melting point of mercury to about 10° above the melting

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[1] This research has been supported in part by the Office of Naval Research. Reproduction, translation, publication, use or disposal in whole or in part by or for the U. S. Government is permitted.

[2] Supported by a grant-in-aid to the Chemistry Department, Princeton University, from E. I. du Pont de Nemours and Company.

[3] C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., New York, N. Y., 1955, pp. 142, 144, 161–163.

[4] C. P. Smyth, ref. 3, pp. 122–125.

[5] For recent measurements and references to previous work, see R. S. Holland, G. N. Roberts and C. P. Smyth, THIS JOURNAL, **78**, 20 (1956).

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

[7] L. Deffet, "Composés Organiques Polymorphes," Editions Desoer, Liège, 1942, p. 15.

[8] C. P. Smyth and C. S. Hitchcock, THIS JOURNAL, **54**, 4631 (1932); **55**, 1830 (1933).

[9] J. D. Hoffman and C. P. Smyth, *ibid.*, **71**, 431 (1949).

point of the substance. Liquid densities at higher temperatures were measured with a Westphal balance. The measurements were carried out with a dilatometer in which a long calibrated capillary was connected to the bottom of a bulb and bent through an angle of 180° to extend vertically above the bulb. A thermometer well extended down into the bulb from the top past its center. The space between the thermometer and the walls of the well was filled with mercury. A weighed quantity of liquid was introduced into the bulb and the remainder of its measured volume was filled with mercury through the capillary tube, thus confining the substance to the upper portion of the bulb. Trapped air was carefully let out from the top of the bulb through a short capillary, which could be closed by a stopcock. The liquid was frozen and melted several times until no further dissolved air was evolved from it. The apparatus was then cooled to the lowest temperature at which it was desired to make measurements and readings of the position of the mercury in the capillary were taken with rising temperature. Readings were taken with rising temperature because the cracks forming in the solid on first cooling were too small for the mercury to enter, while, on further cooling, the cracks opened up sufficiently to permit entry of the mercury and proper determination of the actual volume of the solid. The specific volume was calculated by the equation

$$v = (V_0 + \alpha t - (w_{\mathrm{Hg}}/d_{\mathrm{Hg}}) - AH)/w$$

where

w = weight of substance in dilatometer
V_0 = vol. of dilatometer (22.57 cc. at 0°)
α = coefficient of thermal expansion of glass
t = temperature, °C.
w_{Hg} = weight of mercury
d_{Hg} = density of mercury at temperature of measurement
A = cross-sectional area of capillary (0.0279 cm.^{2})
H = reading of capillary below level at 0°

The cell used in the dielectric measurements was constructed of three coaxial cylinders. On freezing, the liquid in the cell was pulled into the spaces between the electrodes to fill up the voids caused by the contraction due to solidification. Thus at temperatures just below the freezing point, the cell was filled with solid and the dielectric constant measurement was correct. However, on further cooling, voids were formed and since no new material could get into the space between the electrodes, the cracks remained and grew larger as the temperature was further lowered. It can easily be shown, for a condenser consisting of two cylinders of radii a and b, that, if the dielectric shrinks a distance d in from the outer cylinder, the true dielectric constant ϵ is related to the apparent measured dielectric constant ϵ_m by the equation

$$\epsilon = \epsilon_{\mathrm{m}} \left[1 + (\epsilon - 1)\frac{d}{b - a}\right] \qquad (1)$$

where it is assumed that d is small compared to $b - a$, and that $b - a$ is small compared to a, this latter assumption being equivalent to treating the condenser as consisting of parallel plates. Similarly for a crack normal to the plates of the condenser the dielectric constant will be given by equation 2 or 3 depending on whether the crack of width d' or d'' is parallel to the axes or to the circumferences of the cylinders.

$$\epsilon = \epsilon_{\mathrm{m}} \left[1 + \frac{\epsilon - 1}{\epsilon} \times \frac{d'}{2\pi a}\right] \qquad (2)$$

$$\epsilon = \epsilon_{\mathrm{m}} \left[1 + \frac{\epsilon - 1}{\epsilon} \times \frac{d''}{l}\right] \qquad (3)$$

where l is the length of the cylinders. For an isotropic contraction of the material between the plates of the condenser, we have

$$\frac{d}{b - a} = \frac{d'}{2\pi a} = \frac{d''}{l} = \frac{\Delta V}{3V} \qquad (4)$$

where V is the volume of material in the condenser just below the freezing point and ΔV the change in volume that occurs on cooling to the temperature of observation. Combining this expression with equations 1, 2 and 3, we obtain

$$\epsilon = \epsilon_{\mathrm{a}} \left(1 + \frac{(\epsilon + 2)(\epsilon - 1)}{3\epsilon}\frac{\Delta V}{V}\right) = \epsilon_{\mathrm{a}} \left(1 + \beta\frac{\Delta V}{V}\right) \qquad (5)$$

In Fig. 1 the measured dielectric constant of dibromodichloromethane is shown, as is also the specific volume. If β is calculated for the region below the lowest transition, the value 0.85 is obtained. If it is assumed that the polarization in the solid below the lowest transition is equal to the induced polarization obtained from microwave measurements on the liquid, a value of β equal to 1.60 is obtained. This value is nearly that which would be obtained if all the contraction were to take place parallel to the plates (eq. 1) and the resulting strain in the two perpendicular directions were removed by flow. In Fig. 1 is shown the dielectric constant calculated using the value of β = 1.60. In the lower part of the figure is the dipole moment calculated using the Onsager equation and the value of the induced polarization found in the liquid.

Similar results are shown in Fig. 4 for bromotrichloromethane. Since the mercury in the dilatometer freezes at −40°, it was difficult to obtain the specific volume below the transition and the value determined for β = 1.90 may be somewhat in error. This is not important in the interpretation of the results, however, since just below the freezing point where ΔV is still zero, the calculated apparent moment has already dropped to zero.

Discussion of Results

The principal factors determining molecular orientational freedom in the solid as shown by the size of the dielectric constant and in the liquid as shown by the critical wave length[6] would appear to be dipole–dipole and dispersion forces and molecular size and shape, which influence the intermolecular forces. The C–X bond moments (C–F = 1.41, C–Cl = 1.46, C–Br = 1.38, C–I = 1.19) differ little from one another, but C–X dipoles in adjacent molecules approach each other more closely and give larger attractive forces, the smaller the halogen. That these dipole–dipole forces are not sufficient in themselves to prevent molecular rotation is shown by the rotational transition in solid CF_4 (Table II). The attraction by dispersion forces increases with increasing size and consequently increasing polarizability of the halogen, but all four symmetrical CX_4 molecules show rotational transitions.[7] The temperatures at which these transitions occur, like the melting points, rise with increase in molecular size and polarizability. The transition points, 20.4°K. for methane and 22.3° and 27.1°K. for deuteromethane are lower, in accordance with smaller molecular size and polarizability, although their differences from carbon tetrafluoride are not great. Dielectric constant–temperature curves for carbon tetrachloride[10,11]

TABLE II

AXIAL RATIOS, FREEZING POINTS AND TRANSITION POINTS

	Axial ratio (C–X)	F.p., °C.	T.p., °C.
CF_4	1.00	−188.7	−196.9
CCl_4	1.00	− 22.9	− 46.0
CBr_4	1.00	92.3	47.0
CI_4	1.00	170.8	156.8
CCl_2Br_2	1.09	21.8	(10), 0, −13.5
CF_2Cl_2	1.31	−158.2	.....
CF_2Br_2	1.44	−140.1	.....
CF_2BrCl	1.44, 1.31	−159.5	.....
CF_3Br	1.44	−175.5	.....
CF_3Cl	1.31	−189.0	−193.5
CCl_3Br	1.09	− 5.8	−13.5, −34.5
CBr_3Cl	1.09	+ 55	+ 12.5
CCl_3F	1.31	−109.5	.....
CBr_3F	1.44	−74.5	− 88.5

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(10) W. Conner and C. Smyth, THIS JOURNAL, **63**, 3424 (1941).

(11) A. Di Giacomo and C. P. Smyth, *ibid.*, **78**, 2032 (1956).

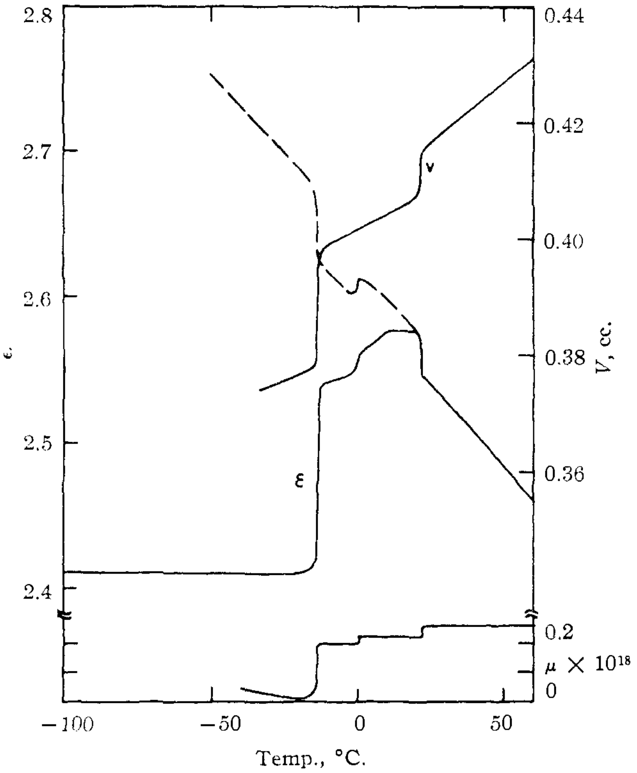

Fig. 1.—Variation with temperature of the measured dielectric constant of dibromodichloromethane, the specific volume and the dielectric constant approximately corrected for the specific volume change (dashed line).

show the transition, but, because of the zero moment of the molecule, do not establish its nature. However, the analogy between the carbon tetrahalide transitions and those in several similar polar substituted methanes and the low values of their entropies of fusion establish them almost certainly as rotational or order–disorder transitions. They are, therefore, listed in Table II as rotational transitions. This table summarizes the freezing and transition points as shown by the dielectric constant–temperature curves in the figures and the ratios of the lengths of the carbon–halogen radii C–X calculated as the sum of the two bond radii plus the van der Waals radius of the halogen, that is, the distance from the carbon nucleus to the hypothetical surface of the halogen atom. The C–X values[12] are as follows: C–F, 2.71; C–Cl, 3.56; C–Br, 3.89; C–I, 4.27 Å. Two of these values are slightly larger and more accurate than those used previously,[6] but the conclusions are not affected by the difference.

Because of the small dipole moments and consequent low dielectric constants of these substances, the dielectric constant values are plotted in the dielectric constant–temperature curves on a larger scale than is usual in such curves, and the effect of density changes may be exceptionally important. The curve for dibromodichloromethane (Fig. 1) shows three transition points in the solid with the possibility of molecular rotational orientation around all axes between the freezing point and the highest transition point and a sharp disappearance of rotational freedom at the lowest transition point. The same transitions have been observed in 3 cm. microwave measurements carried out by Mr. D. E. Williams in this Laboratory and not yet published. When the apparent dielectric constant is corrected for volume change by the method which has been described, the appearance of the dielectric constant–temperature curve (Fig. 1) is completely different. The increase of dielectric constant with decreasing temperature continues in the solid phases almost as rapidly as in the liquid. The molecular dipole moment calculated by means of the Onsager equation, using the value of the optical dielectric constant obtained from the arc plot of microwave measurements,[6] is given in the curve at the bottom of Fig. 1. This shows that the molecular orientational freedom of the solid above the lowest transition point is only a little less than that in the liquid.

The difference in size of the chlorine and bromine atoms as shown by the ratio 1.09 of the van der Waals radii along the C–X axis is so small as to permit the molecular orientation by rotation in dibromodichloroethane, which has been discussed. However, the much larger difference between fluorine and chlorine or bromine evidently prevents rotational orientation of the molecules of the next three substances listed in Table II, the unsymmetrical molecules being too closely packed to permit of rotation. In all three of these substances, the dielectric constant–temperature curve (Figs. 2, 3) drops vertically at the freezing point and rounds off quickly to a straight, almost horizontal line, indicating no molecular orientation freedom. If corrected for density change, this line would, doubtless, rise with falling temperature.

The remaining six substances in Table II are of the type CX_3Y, which might be expected to be capable of some rotation around its axis of symmetry. As the molecular dipole moment lies in this axis, rotation around it should not directly affect the dielectric constant, unless sufficient freedom were involved to permit a precessional motion, which could give a small amount of dipole orientation. The curve for bromotrifluoromethane (Fig. 3) closely resembles those just discussed, dropping sharply at the freezing point to so low a dielectric constant value as to give no evidence of molecular rotation. The curve for chlorotrifluoromethane (Fig. 3) is very similar in form until the slight rounding off is reached at the end of the sharp drop on freezing. At this point, 4.5° below the freezing point, a slight but reproducible nick in the curve indicates a transition, probably involving the cessation of rotational jumps around the C–Cl axis. The low freezing points of these two substances made it impossible to follow the curve for the solid far with liquid nitrogen as a coolant. The curve for tribromofluoromethane (Fig. 2) is very similar to that for chlorotrifluoromethane, indicating similar molecular behavior.

The uncorrected dielectric constant-temperature

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(12) H. A. Stuart, "Die Struktur des Freien Moleküls," Springer, Berlin, 1952, pp. 99, 162.

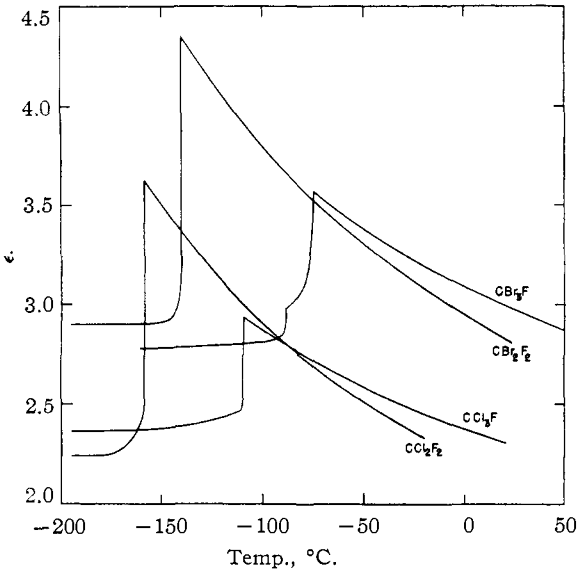

Fig. 2.—Variation of the dielectric constants of dichlorodifluoromethane, dibromodifluoromethane, trichlorofluoromethane and tribromofluoromethane with temperature.

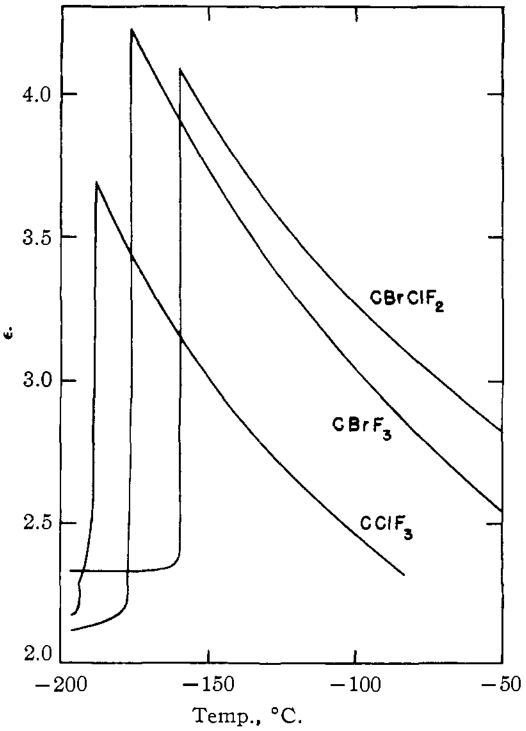

Fig. 3.—Variation of the dielectric constants of bromotrifluoromethane, chlorotrifluoromethane and bromochlorodifluoromethane with temperature.

curve for bromotrichloromethane (Fig. 4) shows two solid state transitions, which are confirmed by the specific volume curve. The uncorrected curve in Fig. 4 might lead to a conclusion of molecular rotational freedom in the solid for 7.7° below the freezing point comparable to that in the liquid, with decrease of freedom at the higher transition point and disappearance below the lower. However, the effective molecular moment calculated as in the case of dibromodichloromethane from the corrected dielectric constants in Fig. 4 and plotted at the bottom of Fig. 4 would seem to indicate virtual cessation of dipole orientation at the freezing point. Nevertheless, the existence of two transitions in the solid and the relatively small departure of the C–X ratio from 1 make reasonably certain the existence of rotation around at least one axis, presumably the C–Br.

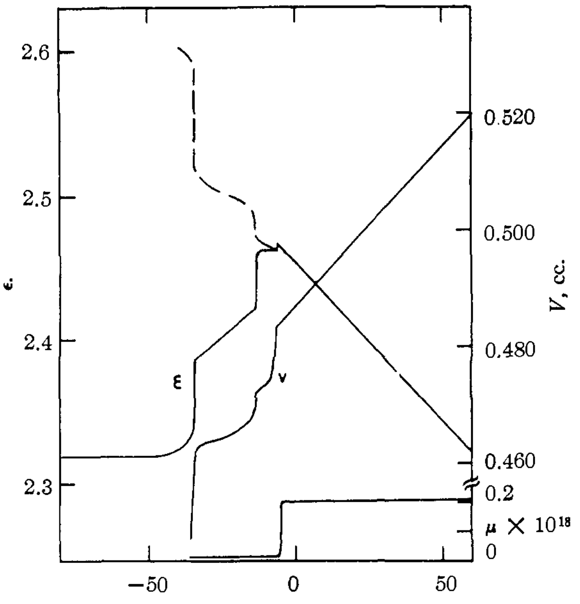

Fig. 4.—Variation with temperature of the measured dielectric constant of bromotrichloromethane, the specific volume and the dielectric constant approximately corrected for specific volume change (dashed line).

The curve in Fig. 5 for tribromochloromethane shows a sharp transition. Unfortunately, repeated shattering of the dilatometer by the solid defeated attempts to measure its density. However, the high value of the dielectric constant of the solid between the freezing point and the transition point indicates probable rotational freedom about all axes, which is consistent with the C–X ratio of 1.09, although the same ratio in bromotrichloro-

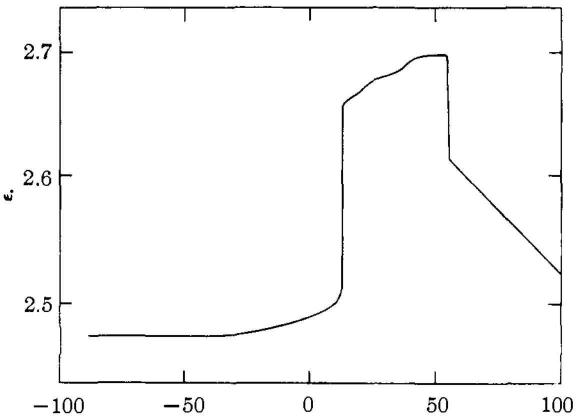

Fig. 5.—Variation of the dielectric constant of tribromochloromethane with temperature.

methane does not give rise to rotational motion around all axes.

The curve for trichlorofluoromethane in Fig. 2 shows no transition in the solid, although the slightly higher than usual dielectric constant of the solid, together with its appreciable decrease with decreasing temperature, suggests some dipole orientational freedom, possibly, arising from loosening caused by rotation around the C–F axis.

When these results are regarded as a whole, it is evident that the rounded-off tetrahedra formed by the molecules of the tetrahalogenated methanes, CX_xY_y, can rotate over hindering potential energy barriers in the crystal lattice in a temperature region extending not far below the melting point, when the ratio of the van der Waals C–X radius to the C–Y radius lies between 1.00 and 1.09. When the ratio is 1.31 or larger, the hindering potential barrier is too high to permit passage by rotational motion. This might be expressed in a different and obvious way by saying that, when one halogen on the central carbon atom exceeds another in "crystal" radius by as much as 33%, and, possibly, by more than 9%, they cannot exchange lattice positions by rotation of the molecule. Of the last six substances in Table II, which have a single threefold axis of symmetry in the molecule, rotation is apparently permitted about this axis in trifluorochloromethane, bromotrichloromethane and tribromofluoromethane above a transition point. For tribromochloromethane, where the ratio is only 1.09, it appears that rotation like that in the CX_4 class is permitted. For trichlorofluoromethane and bromotrifluoromethane, the decrease of dielectric constant with decreasing temperature for some distance below the freezing point suggests the possibility of a gradually decreasing amount of rotation about the axis of symmetry in contrast to a discontinuous transition. The extreme sharpness of the drop in the dielectric constant on freezing of dichlorodifluoromethane (Fig. 2), dibromodifluoromethane (Fig. 2), bromochlorodifluoromethane (Fig. 3) and bromotrifluoromethane (Fig. 3) testifies to the high purity of the materials. It appears, therefore, that some molecular mobility exists for several degrees below the freezing point, as evidenced by the rounding off of the vertical drop of the curves. Since this effect is most pronounced in the symmetrical trichlorofluoromethane, decreases in the less symmetrical dichlorodifluoromethane and dibromodifluoromethane, and is least in unsymmetrical bromochlorodifluoromethane, it seems probable that this is a true lattice property and not the effect of traces of liquid due to impurities. The large effect of specific volume changes upon the shape of the dielectric constant–temperature curve for substances of small molecular dipole moment is shown in the curves for dibromodichloromethane and bromotrichloromethane, which have moments, 0.25×10^{-18} and 0.21×10^{-18}, respectively,[6] and, consequently, small dielectric constants. For substances of large moment and dielectric constant, neglect of volume changes normally does not affect the conclusions to be drawn from the curves.

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[CONTRIBUTION FROM THE LABORATORY OF MOLECULAR STRUCTURE AND SPECTRA, DEPARTMENT OF PHYSICS, THE UNIVERSITY OF CHICAGO]

Hyperconjugation

BY ALF LOFTHUS[1]

RECEIVED JULY 16, 1956

The original work on hyperconjugation of Mulliken, Rieke and Brown has been repeated, including overlap between adjacent atoms, and using some improved assumptions regarding parameters to be used in the semi-empirical LCAO-MO method, and improved empirical data. With the chosen parameters the calculations lead to fairly consistent results for the different examples of conjugated molecules under investigation. The second-order hyperconjugation was found to be small; the contribution is only about 1.4 kcal./mole and 1.1 kcal./mole for a single and double bond, respectively.

Introduction

It has since long been known that groups such as CH_3 and CH_2 should be able to conjugate with multiple bonds. This effect has been called hyperconjugation.[2]

A theoretical approach to the problem of hyperconjugation, based on semi-empirical molecular orbital calculations, was first made by Mulliken, Rieke and Brown.[3] Their basic principle was that two or three ordinary single bonds from a carbon atom to any two or three other atoms may be regarded as constituting a quasi-double or quasi-triple bond whenever there is opportunity for conjugation with a second (quasi or ordinary) multiple linkage. Thus the difference in the conjugation power of $-C{\equiv}H_3$, $-C{\equiv}N$, $-C{\equiv}C-$, etc., are quantitative rather than qualitative in character.

Further, Mulliken, Rieke and Brown classified conjugation in general in the following way

$$\left.\begin{array}{c} HC{\equiv}C{-}C{\equiv}CH \\ N{\equiv}C{-}C{\equiv}N \end{array}\right\} \text{ordinary (first-order) conjugation}$$

$$\left.\begin{array}{c} H_3{\equiv}C{-}C{\equiv}CH \\ H_3{\equiv}C{-}C{\equiv}N \end{array}\right\} \text{second-order conjugation (first-order hyperconjugation)}$$

$$H_3{\equiv}C{-}C{\equiv}H_3 \Big\} \text{third-order conjugation (second-order hyperconjugation)}$$

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[2] For a general review, see V. A. Crawford, *Quart. Rev.*, **3**, 226 (1949), and J. W. Baker: "Hyperconjugation," the Clarendon Press, Oxford, 1952. See also the papers by Mulliken, Rieke and Brown,[3] Coulson and Crawford[5] and I'Haya[6,7] and references cited there.

[3] R. S. Mulliken, C. A. Rieke and W. G. Brown, THIS JOURNAL, **63**, 41 (1941).