[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Dipole Moment and Restricted Rotation in Four Fluorochloroethanes, 1,1,2-Trichloroethane and Chloromethyl Methyl Ether[1,2]

BY ARMAND DI GIACOMO[3] AND CHARLES P. SMYTH

RECEIVED OCTOBER 4, 1954

The dielectric constants of the vapors of 1-chloro-1,1-difluoroethane, 1-fluoro-2-chloroethane, 1,1-difluoro-2,2-dichloroethane, 1,1,2-trichloroethane, 1-fluoro-1,2,2-trichloroethane and chloromethyl methyl ether have been measured over a range of temperature and pressure and used to calculate the molecular dipole moments as functions of temperature. The dipole moment of 1-chloro-1,1-difluoroethane, 2.14×10^{-18}, is independent of temperature, but the moments of the other four ethanes increase with rising temperature. These moment values are used to examine the restriction of rotation of one-half of the molecule relative to the other and to calculate the energy differences between possible rotational isomers. The results are found to compare satisfactorily with the conclusions to be drawn from the potential energy curves calculated as the sums of the energies of steric repulsion, dipole–dipole interaction, London attractive or dispersion forces, and dipole induction between the two halves of the molecule. The moment found for chloromethyl methyl ether is indistinguishable from the value calculated for the case of unrestricted rotation around the central C–O axis and varies so little with temperature as to indicate that change of temperature does not shift the distribution of the molecular halves sufficiently to change the moment appreciably.

The problems of internal rotation around single carbon–carbon bonds have been studied by various experimental methods. Electron diffraction, infrared and Raman spectra, high and low temperature thermochemical measurements and dipole moment measurements have been used to determine either the height of the barrier restricting rotation or the energy difference between rotational isomers. Generally, investigators have dealt with 1,2-disubstituted ethane molecules, of which 1,2-dichloroethane has been most favored. It has seemed of interest, therefore, to investigate several newly available compounds containing fluorine. Measurements carried out by Julian H. Gibbs[4] on chloromethyl methyl ether are included for comparison with the substituted ethanes. 1,1,2-Trichloroethane was measured to reinvestigate a tentatively suggested minimum in its dipole moment *vs.* temperature curve.

Materials and Experimental Methods

1,1-Difluoro-2,2-dichloroethane and 1-fluoro-1,2,2-trichloroethane were obtained from the Halogen Chemicals Company, 1-fluoro-2-chloroethane from the Columbia Organic Chemicals Company, and 1,1,2-trichloroethane from the Eastman Kodak Company. These compounds were purified by distillation through a four-foot column packed with helices, fractions boiling over a 0.1° range being taken for the measurements. Gas from a cylinder of 1-chloro-1,1-difluoroethane kindly given us by the General Chemical Division of the Allied Chemical and Dye Corporation was admitted into the apparatus through towers of ascarite and calcium chloride. Chloromethyl methyl ether, obtained from the Matheson Company, Inc., was dried with calcium chloride and distilled, the middle fraction boiling at 59.5° being used for the measurements.

Molar refractions, R_D, were calculated from refractive indices and densities or from atomic or group refractions in the literature.

The heterodyne beat apparatus and the general experimental technique used to measure the dielectric constants of the vapors have been previously described.[5,6]

Experimental Results

If the polarization values are plotted against the reciprocal of the absolute temperature and the best straight line possible is drawn through them, the polarization at infinite temperature would have the values 33.0 cc. for 1-fluoro-2-chloroethane, 20.3 for 1-chloro-1,1-difluoroethane, 37.0 for 1,1-difluoro-2,2-dichloroethane, 34.6 for 1,1,2-trichloroethane and 35.0 for 1-fluoro-1,2,2-trichloroethane. The molar refractions for the sodium-D line (Table I), which are slightly larger than the electronic polarizations, give for the four ethanes with movable dipoles minimum values for the atomic polarization ranging from 8.7 cc. for 1,1,2-trichloroethane to 16.6 for 1-fluoro-2-chloroethane as compared to 4.3 for 1-chloro-1,1-difluoroethane. From the relatively low value for the latter compound and from considerations of the atomic polarization to be associated with each carbon–halogen dipole,[7] it is seen that the values of the atomic polarization so calculated for the molecules with movable dipoles are too large unless a very considerable moment is produced by internal rotation in the field in addition to that resulting from bending and stretching of bonds. The moments of these compounds, therefore, may not be calculated from the slope of the polarization *vs.* the reciprocal of the absolute temperature. It is necessary to subtract the sum of the electronic and atomic polarizations from the total polarization at each temperature in order to calculate the molecular dipole moment at that temperature. Because of the uncertain and somewhat arbitrary nature of estimating both the electronic and the atomic polarizations from the data generally available, we shall set the sum of the two equal to molar refraction for the sodium-D line in all cases. Although this quantity may be low, the effect of the approximation upon the calculated variation of moment with temperature is small. Thomas and Gwinn[8] have calculated the moment of 1,1,2-trichloroethane over a 157° temperature range and found a variation of 0.07 if nothing is added to R_D for the atomic polarization, and a variation of 0.05 if 3.0 cc. is added.

---

[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 United States Government is permitted.

[2] This article is based upon a portion of a thesis submitted by A. Di Giacomo in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Princeton University.

[3] Procter and Gamble Fellow in Chemistry.

[4] J. H. Gibbs, Ph.D. Thesis, Princeton University, 1950.

[5] K. B. McAlpine and C. P. Smyth, THIS JOURNAL, **55**, 453 (1933); J. M. A. de Bruyne and C. P. Smyth, *ibid.*, **57**, 1203 (1935); J. H. Gibbs and C. P. Smyth, *ibid.*, **73**, 5115 (1951); R. H. Wiswall, Jr., and C. P. Smyth, *J. Chem. Phys.*, **9**, 352 (1942).

[6] C. P. Smyth, "Physical Methods of Organic Chemistry," (A. Weissberger, editor), Vol. I, Part II, Interscience Publishers, New York, N. Y., 1949, Chap. XXIV.

[7] A. Di Giacomo and C. P. Smyth, THIS JOURNAL, **77**, 774 (1955).

[8] J. R. Thomas and W. D. Gwinn, *ibid.*, **71**, 2185 (1949).

TABLE I

MOLAR REFRACTIONS, POLARIZATIONS AND DIPOLE MOMENTS

	T, °K.	P (cc.)	μ ($\times 10^{18}$)
CH_3CF_2Cl	357.1	98.4	
$R_D = 16.6$	393.8	91.7	
P_E(est.) = 16.0	437.6	84.4	
$P_E + P_A = 20.3$	507.1	75.3	
$P_A = 4.3$, $\mu = 2.14$			
CH_2F-CH_2Cl	309.0	82.79	1.84
$R_D = 16.40$	329.4	80.70	1.86
	371.2	76.02	1.91
	418.2	71.26	1.94
	481.7	65.46	1.97
	506.4	63.20	1.97
CHF_2-CHCl_2	333.5	54.12	1.34
$R_D = 21.17$	344.7	53.51	1.35
	357.1	52.70	1.36
	384.7	51.55	1.38
	395.0	51.50	1.40
	428.6	50.66	1.44
	454.7	49.45	1.45
	474.3	49.04	1.47
$CH_2Cl-CHCl_2$	363.6	59.12	1.41
$R_D = 25.85$	388.1	57.49	1.42
	405.9	56.10	1.42
	424.5	56.06	1.45
	444.0	55.35	1.46
	497.2	52.07	1.47
	515.2	51.84	1.48
$CHFCl-CHCl_2$	379.2	56.42	1.38
$R_D = 25.69$	416.6	54.68	1.41
	441.7	53.43	1.42
	474.5	52.31	1.44
	512.0	50.41	1.44
$CH_2Cl-OCH_3$	347.2	89.88	2.03
$R_D = 17.94$	364.8	86.73	2.03
	383.8	83.81	2.04
	384.1	83.49	2.02
	430.0	77.04	2.04
	455.8	73.74	2.04
	466.9	72.95	2.05
	506.8	69.40	2.07

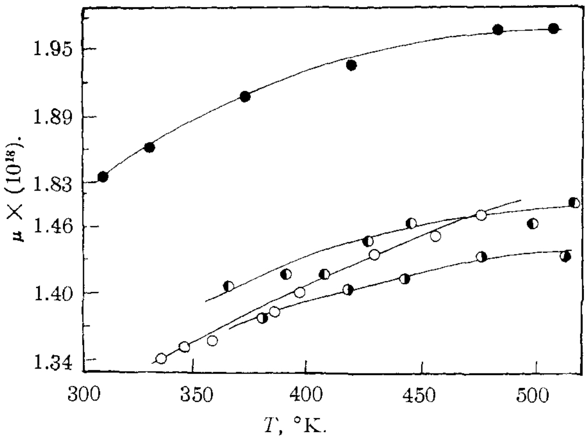

Fig. 1.—Temperature dependence of dipole moments: ●, 1-fluoro-2-chloroethane; ○, 1,1-difluoro-2,2-dichloroethane; ◐, 1,1,2-trichloroethane; ◑, 1-fluoro-1,2,2-trichloroethane.

The dipole moments, except that of chloromethyl methyl ether, calculated as $\mu = 0.01281 \times 10^{-18} [(P - R_D)T]^{1/2}$ are plotted against temperature in Fig. 1.

Discussion of Results

The moment of CH_3CF_2Cl, 2.14, is higher than that of HCF_2Cl[9] 1.40, the difference 0.74 being indistinguishable from that observed[10] for three other cases of $(CH_3CX_3) - (HCX_3)$, *e.g.*, $(CH_3CF_3) - (HCF_3) = 0.73$, $(CH_3CCl_3) - (HCCl_3) = 0.75$, $(CH_3C(NO_2)_3 - (HC(NO_2)_3) = 0.72$. The difference may be attributed to the greater shift of electronic charge from the methyl group toward the negative group, at least part of which shift should result from direct electrostatic induction.

The variable moments of the four substituted ethanes in which the two halves of the molecule can rotate relative to one another around the C–C bond are the resultants of the moments in the two molecular halves. In many of the previous analyses of the moments of such molecules, the potential energy has been taken as determining the distribution of the molecules among an infinite number of positions of rotation around the C–C axis designated by the value of ϕ, the azimuthal angle between the projections in a plane perpendicular to the C–C bond of the resultant vectors of the dipoles on each of the two ethane carbons. For simplicity of calculation the potential energy has often been represented by the function

$$V(\phi) = (V_0/2)(1 + \cos \phi) \qquad (1)$$

Although this is an extreme over-simplification, it has been used on the present results by the method previously described[11] to calculate from the moment value at each temperature a value of V_0, the height of the hypothetical single potential energy barrier hindering free rotation of one-half of the molecule relative to the other. The values thus obtained show a rise of V_0 of 10 to 25% over the ranges of temperature used in the measurements. The details of the calculation and the individual values obtained are given elsewhere.[10] The average value of V_0 is given in Table II for each substance.

TABLE II

POTENTIAL ENERGY BARRIERS, V_0 AND ΔU, AND DIFFERENCES, ΔE (KCAL./MOLE)

			ΔE from:		
	V_0	ΔU	μ, m_s and m_t	μ and m_s or m_t	Pot. curve
CH_2F-CH_2Cl	1.3	2.7	0.67	0.46	0.48
CHF_2-CHCl_2	1.9	3.8	1.1	.71	.50
$CH_2Cl-CHCl_2$	2.6	5.5	2.6	3.0	3.2
$CHFCl-CHCl_2$	1.9	6.4	3.0	2.0	2.6

The total potential energy

$$U = U_s + U_m + U_i + U_d \qquad (2)$$

between the two halves of the molecule has been calculated as a function of ϕ. U_s, the energy of steric repulsion, U_d, the energy of London attractive or dispersion forces, U_i, the energy of dipole induction, and U_m, the energy of dipole–dipole re-

---

(9) C. P. Smyth and K. B. McAlpine, *J. Chem. Phys.*, **1**, 190 (1933).

(10) A. Di Giacomo, Ph.D. Thesis, Princeton University, 1953.

(11) J. Y. Beach and D. P. Stevenson, *J. Chem. Phys.*, **6**, 635 (1938).

pulsion, have been calculated as functions of ϕ by methods similar to those previously described.[12] The details of the calculations and the values of all the quantities for values of ϕ at 10° intervals are given elsewhere.[10] U is calculated as the sum of the component energies and plotted in Fig. 2 as a function of the angle of rotation, ρ, defined by the angles between the projections of the two halves of each molecule shown in Fig. 2.

The average value of V_0 for 1-fluoro-2-chloroethane, 1.3 kcal., is much lower than the value, 3.2 kcal., calculated for 1,2-dichloroethane by Oriani and Smyth.[13] This is to be expected in view of the smaller size of the fluorine atom, and is further reflected in the fact that, while both compounds should have about equal free rotation moments of about 2.5×10^{-18}, the moment of 1-fluoro-2-chloethane at any temperature is larger than that of 1,2-dichloroethane at the same temperature[14] and its rate of change is much less (0.7×10^{-21} per degree as compared with 1.7×10^{-21}).[14] The value of V_0 for 1,1,2-trichloroethane, 2.6, is in satisfactory agreement with the value 2.8 reported by Oriani and Smyth.[13] The moment is seen to rise continuously with temperature from 1.41 at 364°K. to 1.48 at 515°K. giving no evidence of the slight minimum which appeared in the previous measurements.[13,15] This minimum was ultimately concluded to be within the experimental error and the values were averaged to give 1.43, with which the average of the values in Table I, 1.44, is in good agreement. The fact that the barrier in 1,1-difluoro-2,2-dichloroethane, 1.9 kcal., is less than that in 1,1,2-trichloroethane shows that, in the eclipsed form, the interaction of two chlorine–fluorine pairs is not as great as that between a chlorine–chlorine plus a chlorine–hydrogen, in addition to which, in the configuration of low energy the halogens are nearer to each other in the difluoro compound than in the trichloroethane, causing the energy in the former compound to be slightly greater than in the latter. The potential barrier V_0 of 1-fluoro-1,2,2-trichloroethane has the surprisingly low value of 1.9 kcal., whereas one would have expected it to be greater than the barrier of 1,1,2-trichloroethane. The reason for the discrepancy is probably due to the configuration at $\rho = 280°$, which has low energy and large moment. Consequently, the dipole moment measured at any temperature is larger than it would otherwise be, resulting in too small a calculated value for V_0. In Table II, the difference $\Delta U = U(0°) - U(180°)$ is 2.7 kcal. for 1-fluoro-2-chloroethane and 3.8 kcal. for 1,1-difluoro-2,2-dichloroethane. In the calculated U curve for 1,1,2-trichloroethane (Fig. 2) the lower minimum occurs at $\rho = 210°$ and again at 270° separated by a hill of only 0.3 kcal. at 240°; the maximum occurs at 120° and at 360° (or 0°). The energy difference is, therefore, $\Delta U = U(0°) - U(210°)$, which equals 5.5 kcal. (Table II).

It is interesting to note that the ratio $V_0:\Delta U$ is very close to one-half in three cases. In other words, the relative heights of the potential barriers given by the cosine function are in good agreement with the relative values of the theoretically calculated potential barriers. However, in the case of 1-fluoro-1,2,2-trichloroethane, $\Delta U = U(0°) - U(190°) = 6.4$ kcal., whereas V_0, for the reason suggested above, has the low value of 1.9 kcal.

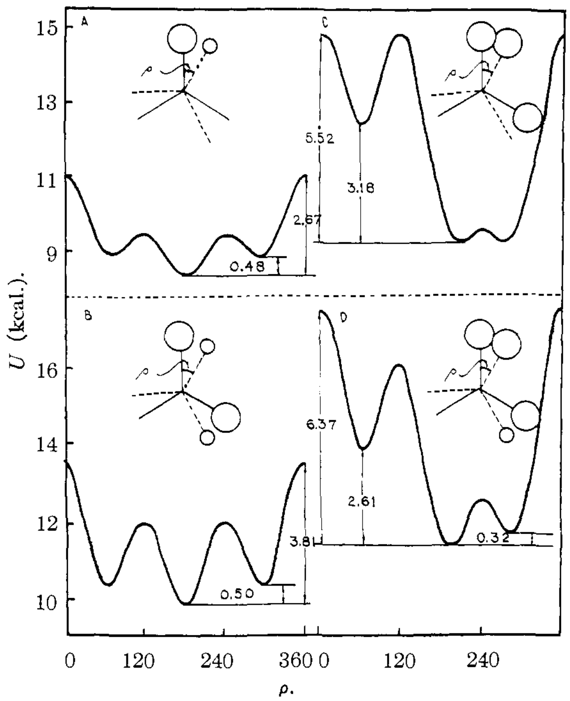

Fig. 2.—Potential energy as a function of angle of rotation: A, 1-fluoro-2-chloroethane; B, 1,1-difluoro-2,2-dichloroethane; C, 1,1,2-trichloroethane; D, 1-fluoro-1,2,2-trichloroethane.

If we consider these molecules to exist only in a configuration corresponding to one or other of the wells of the potential energy curve, then the ratio of the fractions of molecules in the skew, or staggered, and the *trans* forms is

$$N_s/N_t = wf \exp[-\Delta E/RT] \quad (3)$$

where ΔE is the energy difference between these two forms, f is the ratio of their partition functions, which may be taken as approximately unity, and w the ratio of their *a priori* probabilities or statistical weights. We may express the mean moment, m, in terms of the moments of skew and *trans* forms as

$$m^2 = N_s m_s^2 + N_t m_t^2 \quad (4)$$

Remembering that $N_s + N_t = 1$, one may rearrange eq. 4 to yield

$$N_s/N_t = (m^2 - m_t^2)/(m_s^2 - m^2) \quad (5)$$

Combining eq. 3 and 5, and setting f equal to unity, we obtain

$$(m^2 - m_t^2)/(m_s^2 - m^2) = w \exp[-\Delta E/RT] \quad (6)$$

Approximate values for m_t and m_s may be calculated from the observed moments of methyl fluoride, methyl chloride, dimethyl ether, etc., after allowing for mutual inductive effects. By doing so, and utilizing the observed moment at a single temperature, values of ΔE were calculated at each temperature for the substituted ethanes. In these calculations, w was set equal to 2 in 1-fluoro-2-chloroethane and

---

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

(13) R. A. Oriani and C. P. Smyth, *ibid.*, **17**, 1174 (1949).

(14) C. T. Zahn, *Phys. Rev.*, **40**, 291 (1932).

(15) R. A. Oriani and C. P. Smyth, *J. Chem. Phys.*, **16**, 930 (1948).

1,1-difluoro-2,2-dichloroethane and equal to $^1/_2$ in the other two compounds. The average value of ΔE thus obtained for each molecule is listed in the fourth column of Table II. The values are approximate because, in some instances, they depend very strongly upon the precise values of m_s and m_t used in the calculation. To take an extreme example, ΔE for 1,1,2-trichloroethane may be reduced from 2.6 to 1.3 kcal. by assuming for m_t a value of 1.16×10^{-18} instead of 1.38×10^{-18}, which corresponds to $\phi = 140°$ rather than $\phi = 130°$. It is possible somewhat to reduce this arbitrary feature of the calculation by solving eq. 6 for ΔE and either m_s or m_t, using the dipole moments observed at each of two temperatures. The ΔE values so calculated and averaged to give the values tabulated in the fifth column of Table II deviate less from the mean and are in better agreement with the energy differences between rotational isomers given by Fig. 2 and listed in the last column of Table II.

In 1-fluoro-2-chloroethane, the moment of the *trans* configuration cannot but be very close to zero. With the aid of the moments observed experimentally at the highest and lowest temperatures investigated, m_s was calculated as 2.65×10^{-18}, which is quite close, as it should be, to the corresponding value, 2.55×10^{-18}, of 1,2-dichloroethane.[16] The values for the energy differences between isomers calculated at the various temperatures, are in excellent agreement with each other, and the mean is seen to agree well with the value 0.48 kcal. given by the curve, which must be regarded as somewhat fortuitous in view of the uncertainties in the calculations. The value for 1-fluoro-2-chloroethane of 0.48 kcal. is smaller than 1.21 kcal. found by Mizushima, *et al.*,[16] by a similar calculation on 1,2-dichloroethane, as might have been expected. As discussed above in connection with the heights of the potential barrier in these two compounds, their experimental moments are entirely consistent with the fact that energy differences (now between rotational isomers) should be less in the case of the fluoro compound.

In general, the values for the energy differences between the rotational isomers as calculated from the dipole moment data, and the values obtained from the calculated potential energy curves are seen to be in rough agreement with each other despite the approximate nature of the calculations.

The chloromethyl methyl ether molecule may be treated as consisting of two halves, ClH_2C and OCH_3, which may rotate relative to each other around the C–O axis, just as the ethylene chloride molecule has been treated as consisting of two halves, ClH_2C and CH_2Cl, which may rotate relative to each other around the C–C axis. There is, however, a marked difference between the two molecules in that the resultant dipoles in both halves of the $ClH_2C–CH_2Cl$ have their positive ends toward the axis of rotation, while, in the $ClH_2C–OCH_3$ molecule, the ClH_2C half has its positive end toward the axis of rotation, and the OCH_3 half has its negative end toward the rotation axis. The potential energy has not been calculated as a function of ϕ for this molecule, but it is evident that, when the chlorine and the methyl are in *cis* positions relative to each other, the energy of dipole–dipole interaction is negative and opposite in sign to that of steric repulsion, which is positive. Since U_i and U_d are negative throughout, the potential curve should be rather flat. Moreover, the *trans* position is the position of maximum moment, instead of the *cis* position. One would, therefore, expect a lower dependence of moment on temperature than is usually observed for molecules with mutually rotatable dipoles. This expectation is confirmed by the moment values in Table I, which increase only from 2.03 to 2.07 over a 160° range of temperature. Since the polarization from which the 2.07 value is calculated lies slightly above the $P - 1/T$ curve, the increase is probably only from 2.03 to 2.05. The $P - 1/T$ line at $1/T = 0$ gives an intercept, $P_E + P_A = 22.5$, which gives an apparent P_A value, 5.2 cc., with a corresponding moment value, 1.97. The value calculated by Dr. J. H. Gibbs[4] from the geometry of the molecule on the assumption of equal probability for all values of ϕ, that is, free rotation around the C–O axis, is 1.98, which is indistinguishable from the experimental values. Actually, this should not be interpreted as meaning a complete absence of potential energy variation with change in ϕ, but rather that variation of the resultant moment with ϕ is small and that change of temperature does not shift the distribution of the molecular halves among different relatively stable positions sufficiently to change the moment by more than 0.02–0.03 within the 160° range of temperature experimentally attainable.

PRINCETON, NEW JERSEY

---

(16) S. Mizushima, *et al.*, *J. Chem. Phys.*, **17**, 591 (1949).