a solution in 50% aqueous alcohol absorbed no alkali on titration. A few milligrams of the compound was refluxed for forty-five minutes with 1 *N* ethyl alcoholic potassium hydroxide solution after which the solution was poured into water. No precipitation occurred but acidification with hydrochloric acid precipitated a compound which after solution in 50% alcohol absorbed no alkali on titration. These properties indicate that the neutral product is a lactone diacetate which is saponified by alcoholic alkali to a dihydroxy lactone.

Anal. Calcd. for $C_{26}H_{38}O_6$: C, 69.93; H, 6.58. Calcd. for $C_{26}H_{38}O_6 \cdot CH_3OH$: C, 67.76; H, 8.84. Calcd. for $C_{27}H_{44}O_7$: C, 67.46; H, 9.26. Found: C, 67.85; H, 9.36.

Attempts to determine the equivalent weight of the lactone diacetate by saponifying with an excess of standard alkali and back titrating did not give consistent results due to the hydrolysis of the sodium salt and reformation of the lactone. The **dihydroxy lactone** recovered from these saponifications consisted of needles, m. p. 255–256°.

Anal. Calcd. for $C_{22}H_{34}O_4$: C, 72.88; H, 9.46. Calcd. for $C_{22}H_{34}O_4 \cdot CH_3OH$: C, 70.01; H, 9.71. Calcd. for $C_{23}H_{40}O_5$: C, 69.66; H, 10.17. Found: C, 69.62; H, 10.01.

Oxidation of Chlorogenoic Acid Diacetate.—Of the many attempts made to obtain intermediate oxidation products between the acid and the lactone, the most successful was the oxidation with potassium permanganate. A neutral solution of the sodium salt from 0.1 g. of chlorogenoic acid diacetate was refluxed for thirty minutes with an aqueous solution of 0.038 g. of potassium permanganate. Precipitation of manganese dioxide began almost immediately and the purple color disappeared in a few minutes. After thirty minutes, the solution was filtered and the precipitate washed well with water. Acidification of the filtrate gave a flocculent white precipitate, m. p. 175–190°. After two crystallizations from 70% aqueous acetone and one from acetone it melted at 221–222°. The compound is much more soluble in 70% aqueous acetone than in acetone alone but is precipitated from the 70% acetone on further dilution with water.

Anal. Calcd. for $C_{27}H_{42}O_6$: C, 70.09; H, 9.16; neut. equiv., 462.6. Found: C, 69.81, 70.05; H, 9.23, 8.85; neut. equiv., 484.

The same acid was isolated in small amounts after oxidation of the sodium salt with hydrated manganese dioxide at 65–70° and in one of the chromic oxide oxidations at 40°. In none of the oxidations yielding this acid could the results be duplicated consistently since the acid appears to undergo further oxidation with the formation of oils and gums that could not be crystallized. Chlorogenoic acid diacetate was recovered unchanged after treatment in acetic acid solution with lead tetraacetate.

Cleavage of the Side Chain of Chlorogenin.—A fragrant oil was obtained on treating 10 g. of chlorogenin with acetic acid–hydrochloric acid according to the procedure of Jacobs and Simpson.[5] This was converted into a semicarbazone but extreme difficulty was encountered in attempting to isolate a pure product. Recrystallization from ether–petroleum ether mixtures failed to give a product melting above 100°. A large number of other solvents and solvent mixtures were tried without success. By passing an ether solution of the semicarbazone through a column packed with a mixture of magnesium oxide and Celite, evaporating successive portions of the filtrate separately and rubbing up the solid residues with small amounts of ether, a product was obtained from the middle fractions that melted at 114–118°. This material consisted of tiny microcrystals but was still somewhat gummy and could not be purified further by crystallization. The melting point given by Jacobs and Simpson for the semicarbazone of the ketone from sarsasapogenin and gitogenin is 119.5–120°.

Summary

Oxidative and acid degradation of chlorogenin indicates that the structure of the side chain is very similar to, if not identical with, that of the other steroid sapogenins.

STANFORD UNIVERSITY, CALIF. RECEIVED MAY 10, 1938

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC CO.]

Dielectric Constants of Some Fluorine Compounds

BY RAYMOND M. FUOSS

I. Introduction.—In contrast to the other halogens, the properties of fluorine compounds have been studied comparatively little. Recent technical interest in new refrigerants has, however, made a large number of fluorinated methanes and ethanes available. Below are presented the results of an investigation of the dielectric constants of fifteen fluorine compounds.

II. Materials, Apparatus and Method.—The fluorine compounds were presented to us by the Jackson Laboratory of E. I. du Pont de Nemours and Company, to whom grateful acknowledgment is made.

The bench apparatus consisted of a manifold to which were connected an oil pump, three distilling bulbs with an ascarite tube between the first two, a manometer and a guarded condenser. The ascarite served to remove traces of water or of hydrogen halides which might have been present. The stopcocks were lubricated with a sirup of phosphoric acid and anhydride for the higher boiling compounds; ordinary heavy grease was used for the others. The samples were distilled from the supply cartridges into the first bulb, and then distilled back and forth through the ascarite. After each of the first few condensations, the samples were pumped to remove small amounts of dissolved air. Then the sample was distilled from the first bulb in small portions, and a dielectric constant determination at several pressures was made on each portion. The third bulb was used as a receiver for the initial and final portions, so that the middle fraction could be redistilled to give a check determination. The vapor density of the middle fraction was determined by weighing against a matched counterpoise a bulb (volume 421.3 cc.) filled with the gas at known pressures and temperature.

The measuring condenser was a 100 $\mu\mu$f radio condenser mounted in a vacuum-tight brass case, and insulated from the latter by mica washers. The case was connected to the guard line in the Schering bridge circuit.[1] The leads (high potential and test) to the condenser plates were brought out as tungsten wires through glass insulation fused to fernico tubes which were soldered to the brass case. The condenser case was connected to the manifold by a graded seal between a fernico bushing and the Nonex glass of the manifold. The insulation between the two sets of brass condenser plates was isolantite; the insulation held up very well, but in the course of about six weeks use developed a slightly conducting film. (The original value of tan δ at 60 cycles for the cell was 0.0004; during use, it gradually rose to 0.0014.) The cell was mounted in a wooden box in order to surround it by a dead air space; the cell temperature was determined by means of a thermocouple inserted in a well soldered inside the case.

All measurements were made at 60 cycles and 100 v. across the cell. The temperature varied from about 22 to 30°, depending on room temperature, but the drift in any run was so slow that no appreciable error was introduced due to uncertainty in temperature for a given reading.

The polarization was obtained in several ways from the data, which consisted in a series of pressure and resistance measurements. Since the unknown arm of the bridge was substantially loss free, we have

$$C_x = SR_4/R_3 \qquad (1)$$

where C_x is the unknown capacity, S is a 100 $\mu\mu$f standard capacity and R_4 and R_3 are the other two components of the bridge network. But the dielectric constant ϵ' is given by

$$\epsilon' = C_x/C_0 \qquad (2)$$

where C_0 is the capacity of the evacuated condenser. In turn

$$C_0 = SR_4^0/R_3^0 \qquad (3)$$

In the measurements, R_3 was kept fixed for all readings on a given compound, so that R_3 and S dropped out of the final result

$$\epsilon' = R_4/R_4^0 \qquad (4)$$

R_3 was selected to make R_4^0 just above 10,000 ohms, so the bridge was made direct reading in dielectric constant

$$\epsilon' = 1 + 10^{-4}\Delta R_4 \qquad (5)$$

where ΔR_4 was the difference between R_4^0 for the evacuated cell and R_4 for the cell filled with gas at pressure p. R_4 could be determined to ±0.2 Ω which gives an accuracy of about ±0.002% in ϵ'. The polarization P was calculated by the Clausius–Mosotti formula

$$P = \frac{\epsilon' - 1}{\epsilon' + 2}\frac{M}{\rho} \qquad (6)$$

where M is the molecular weight and ρ is the density, for the temperature and pressure at which ϵ' was determined. As a check on the consistency of the results $(\epsilon' - 1)/p$ was plotted against p, and P was calculated, using the ideal gas density[2] as follows

$$P = 2.097 \times 10^4\, T \lim_{p \to 0}\left(\frac{\epsilon' - 1}{p_{\text{mm.}}}\right) \qquad (7)$$

Finally, a value of P was calculated from the low pressure data (where the deviations from ideal behavior were small) by the formula

$$P = 2.079\, T\,(\Delta R_4/\Delta p) \qquad (8)$$

All pressures were corrected to 0° by the formula

$$p_0 = p\,(1 - 0.000175t) \qquad (9)$$

Values of P calculated by (6), (7) and (8) for a given compound usually agreed within several per cent. or better. Lack of agreement was an indication of impurities in the sample, because (6) contains the actual density of the sample while (7) and (8) contain only the ideal gas density.

III. Results.—An abstract of the experimental results is given in Table I. The pressures have been corrected to millimeters at 0° and rounded off to three places. In order to make the tables more compact, the dielectric deviation δ is given in place of the dielectric constant ϵ'; the two are related by the equation

$$\epsilon' = 1 + 10^{-8}\,\delta \qquad (10)$$

In Fig. 1 are given some examples of $\epsilon' - p$ curves, which illustrate the method of determining polarization by means of (8). It should be pointed out that the scattering of the points from the straight lines of Fig. 1 is a direct measure of the reproducibility of the Schering bridge readings; one unit in the δ-scale corresponds to 10 Ω in R_4. The absolute values of ϵ' are consistent to about ±0.002%, *i. e.*, several units in the fifth place.

Figure 2 illustrates the evaluation of polarization by means of the extrapolation of $(\epsilon' - 1)/p$ to zero pressure. As is well known, the limiting value of $(\epsilon' - 1)/p$ permits P to be calculated using ideal gas densities. It was, however, considered desirable in this work to make direct de-

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(1) Fuoss, THIS JOURNAL, **59**, 1703 (1937).

(2) Fuchs, *Z. Physik* **63**, 824 (1930).

TABLE I

DIELECTRIC CONSTANTS OF FLUORINE COMPOUNDS

p	δ	p	δ	p	δ
SF_6, t = 27.5°		CF_2Cl_2, t = 29.0		CHF_2Br, t = 27.2°	
708	1.91	719	3.05	734	7.29
704	1.90	504	2.14	682	6.79
590	1.58	417	1.76	654	6.45
457	1.23	331	1.41	461	4.52
369	0.98	188	0.79	419	4.02
216	.57	157	.65	324	3.13
131	.34	83	.32	214	2.07
				129	1.23
				86	0.83
CF_4, t = 24.8°		$CFCl_3$, t = 26.0°		$CHFCl_2$, t = 30.0°	
723	1.13	498	2.51	719	6.59
629	0.98	448	2.24	709	6.51
515	.81	339	1.67	419	3.79
429	.67	270	1.32	312	2.80
332	.52	189	0.92	222	1.99
223	.36	129	.60	134	1.20
131	.21	73	.35		
CF_3Cl, t = 29.0°		CHF_2Cl, t = 25.4°		CF_2Br_2, t = 28.8°	
619	1.96	711	6.58	718	5.03
607	1.93	611	5.64	652	4.53
484	1.53	509	4.69	617	4.28
330	1.00	410	3.74	519	3.49
211	0.66	311	2.82	411	2.72
99	.31	205	1.87	299	1.99
		154	1.37	210	1.45
		105	0.96	114	0.82
		82	.72	64	.45
CF_3CF_3, t = 23.0°		$CClF_2CClF_2$, t = 26.8°		CH_3CF_3, t = 25.2°	
711	1.97	715	4.04	644	13.23
608	1.69	605	3.40	554	11.34
509	1.40	512	2.87	436	8.91
411	1.14	416	2.30	337	6.83
307	0.86	328	1.80	219	4.43
201	.56	225	1.25	120	2.42
110	.31	150	0.83	83	1.67
61	.17	93	.52	61	1.23
		63	.34	40	0.82
				24	.47
CF_3CF_2Cl, t = 27.4°		$C_2H_2ClF_3$, t = 26.6°		CH_3CClF_2, t = 27.4°	
722	3.34	715	10.25	706	13.38
584	2.71	612	8.74	600	11.31
506	2.36	513	7.30	511	9.59
333	1.58	414	5.86	379	7.09
260	1.23	309	4.37	279	5.21
195	0.93	207	2.95	204	3.79
121	.58	153	2.19	155	2.89
59	.28	107	1.53	123	2.29
		65	0.91	95	1.77
		43	.60	71	1.33
				47	0.87
				34	.64

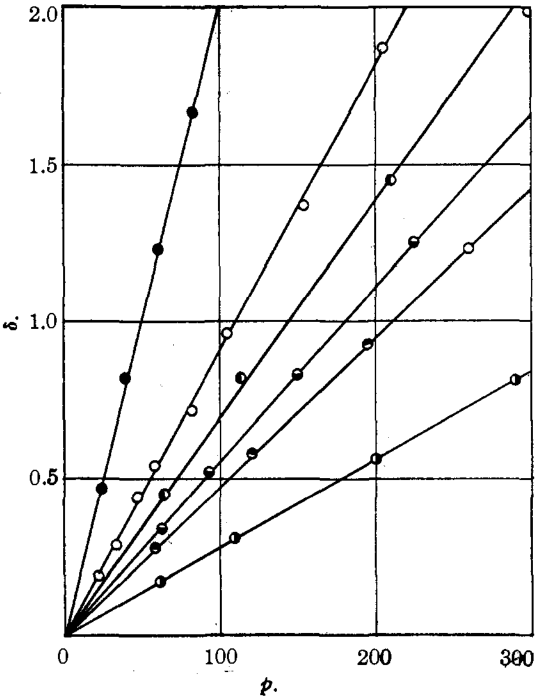

Fig. 1.—Change of dielectric constant with pressure: ◐, CF_2Br_2; ◑, C_2F_6; ●, CH_3CF_3; ◒, $C_2Cl_2F_4$; ◓, C_2ClF_5; ○, CHF_2Cl.

terminations of the vapor densities, in order to check the purity of the samples. The results of the vapor density determinations are given in Table II. The first column gives the formula of the compound, the next two the pressure and temperature corresponding to the density (in mg./cc.) in the fourth column, and the fifth column gives the ratio of the apparent molecular weight to that calculated from the chemical formula. Gases of the type discussed here should give positive deviations up to several per cent.

TABLE II

VAPOR DENSITIES AND POLARIZATIONS OF FLUORINE COMPOUNDS

Compound	p	t	ρ	M/M_0	t	P
SF_6	718.8	27.8	5.650	1.0102	27.5	16.8
CF_4	722.9	23.6	3.451	1.0039	24.8	9.7
CF_3Cl	613.8	28.3	3.430	1.0058	29.0	19.8
CF_2Cl_2	719.3	28.0	4.709	1.0169	29.0	26.2
$CFCl_3$	551.2	27.2	4.138	1.0238	26.0	30.7
CHF_2Cl	711.2	25.4	3.377	1.0223	25.4	56.1
CHF_2Br	466.8	27.0	3.129	0.9584	27.0	60.0
$CHFCl_2$	712.8	29.2	3.958	1.0172	30.0	56.5
CF_2Br_2	654.8	28.6	7.426	1.0172	29.0	43.0
CH_3CF_3	644.2	26.0	2.948	1.0161	25.2	124.2
CH_3CClF_2	706.8	26.6	3.895	1.0252	27.4	115.5
CF_3CF_3	710.5	22.6	5.335	1.0036	22.6	17.2
CF_3CF_2Cl	721.8	27.0	6.007	1.0092	26.2	28.7
$CClF_2CClF_2$	715.2	26.2	6.569	1.0047	26.2	34.5
$C_2H_2ClF_3$	715.6	26.2	4.776	1.0516	26.2	83.6

from ideal behavior. The sixth column gives the temperature at which the polarization was calculated; the polarization is given in the last column. The figure given is an average, based on the direct determinations and on the extrapolated values.

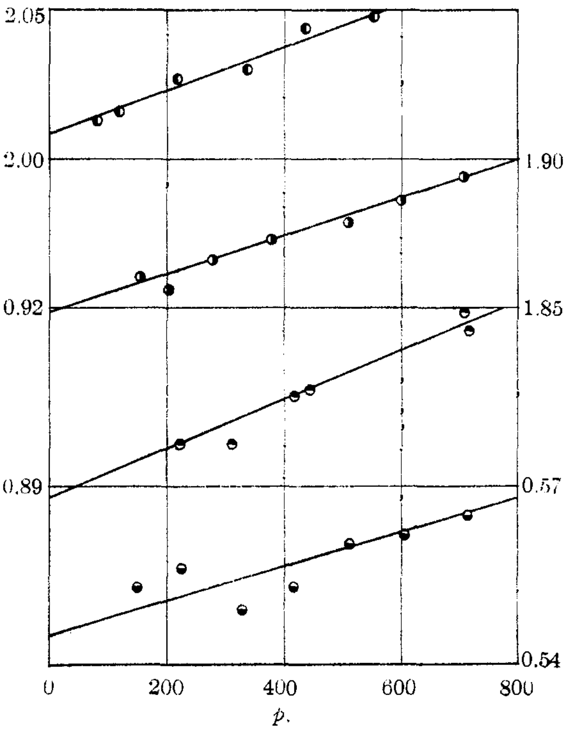

Fig. 2.—Variation of $(\epsilon' - 1)/p$ with pressure: ◐, CH_3CF_3; ◑, CH_3CClF_2; ◓, $CHFCl_2$; ◒, $C_2Cl_2F_4$.

IV. Discussion.—We begin by comparing the results of Table II with previously observed values for the cases where they are available. For SF_6, Watson, Rao and Ramaswany[3] find $P_{25°}$ = 16.51 cc. and for CF_4, Watson, Kane and Ramaswany[4] find $P_{25°}$ = 10.15 cc.

Four of the fluorinated chloromethanes have been studied by Smyth and McAlpine[5] at a series of temperatures, which permitted a direct determination of P_M, the part of the polarization due to orientation of permanent dipoles. Since the total polarization P is given by

$$P = P_E + P_A + P_M \qquad (11)$$

we can calculate values of the moments from the data of Table II by using Smyth's values for P_A, the atomic polarization, together with calculated values for P_E, the electronic polarization. For the latter, the following values of atomic refractivities, extrapolated to infinite wave length by the Cauchy formula,[6] were used: C = 2.37, H = 1.07, Cl = 5.80, Br = 8.53, F = 1.00. The first four figures are conventionally accepted; for fluorine, whose atomic refraction varies with the compound containing it,[7] an average value was chosen which was derived from compounds of the type studied here.[4,7–10] An average value for P_A = 4.0 cc. was used for the fluoromethanes; Smyth and McAlpine's value 0.9 for $CHFCl_2$ seems low compared to the values they find for the other three compounds and to Watson's value of 2.86 for CF_4. We obtain the results given in Table III, where the moments are given in Debye units.

TABLE III

DIPOLE MOMENTS OF FLUOROMETHANES

Compound	(R. M. F.)	(S. and McA.)
CF_4	0.0	—
CF_3Cl	.47	—
CF_2Cl_2	.55	0.51
$CFCl_3$	.53	.45
CHF_2Cl	1.41	1.40
$CHFCl_2$	1.34	1.29
CHF_2Br	1.30	—
CF_2Br_2	0.72	—

It will be seen that the agreement is within the experimental error of the writer's method; the method of Smyth and McAlpine gives one more significant figure in the dielectric constant.

We can compare the result for CF_3Cl with that for the other fluorochloromethanes by the method of vector addition used by Smyth and McAlpine. Using their notation, in which the symbol for a radical or molecule in parentheses denotes its dipole moment corrected for induction,[11] we have

$$\begin{aligned}(CF_3Cl) &= 3(C - F)\cos 70° - (CCl)\\ &= (CF) - (CCl) = 0.47 \text{ (obsd.)}\\ (CFCl_3) &= (CF) - 3(CCl)\cos 70°\\ &= (CF) - (CCl) = 0.53 \text{ (obsd.)}\\ &= 0.45 \text{ (Smyth and McAlpine)}\end{aligned}$$

The moments of the last two compounds in Table III give a value for the difference (CCl) − (CBr). We shall assume an atomic polarization of 11.0 cc. for the bromo compounds; this value was chosen after considering the few data available on atomic polarization of bromoalkanes.

$$\begin{aligned}(CHF_2Br) &= (CH) + {}^1/_3(2CF + CBr) = 1.30\\ (CHF_2Cl) &= (CH) + {}^1/_3(2CF + CCl) = 1.41\end{aligned}$$

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(3) Watson, Rao and Ramaswany, *Proc. Roy. Soc.* (London), **143**, 558 (1934).

(4) Watson, Kane and Ramaswany, *ibid.*, **156**, 130 (1933).

(5) Smyth and McAlpine, *J. Chem. Phys.*, **1**, 190 (1933).

(6) Smyth, *Phil. Mag.*, **45**, 849 (1923).

(7) Swarts, *J. chim. phys.*, **20**, 30 (1923).

(8) Klemm and Henkel, *Z. anorg. allgem. Chem.*, **213**, 115 (1933).

(9) Locke, Brode and Henne, THIS JOURNAL, **56**, 1726 (1934).

(10) Henne and Renoll, *ibid.*, **58**, 887 (1936).

(11) Smallwood and Herzfeld, *ibid.*, **52**, 1919 (1930).

whence (CCl) − (CBr) = 0.33, and

$$(CF_2Br_2) = (CF) - {}^1/_3(CF + 2CBr) = 0.72$$
$$(CF_2Cl_2) = (CF) - {}^1/_3(CF + 2CCl) = 0.55$$

whence (CCl) − (CBr) = 0.26. When compared with Morgan and Lowry's[12] value for methyl bromide, it appears that the results for both the bromo compounds are high by about the same amount, as is shown by the following calculation

$$(CHF_2Br) = (CH) + {}^1/_3(2CF + CBr) = 1.30 \text{ (obsd.)}$$
$$(CF_2Br_2) = (CBr) - {}^1/_3(2CF + CBr) = 0.72 \text{ (obsd.)}$$
$$(CH) + (CBr) = 2.02$$
$$(CH_3Br) = (CH) + (CBr) = 1.45 \text{ (Morgan)}$$

The agreement could, of course, be improved by assigning a larger value to P_A for CF_2Br_2, which would also improve the agreement between the two determinations of the (CCl) − (CBr) difference. However, the available samples of these two compounds were quite small and did not permit a careful fractionation; judging from the vapor density, the CHF_2Br contained an impurity of low molecular weight. The value 11.0 cc. used above for P_A already seems large. If a smaller value is chosen, the following values are obtained: with $P_A = 4.0$ cc. $\mu(CHF_2Br) = 1.43$ and $\mu(CF_2Br_2) = 0.93$, which gives (CH) + (CBr) = 2.36, a value which seems entirely too large. Until data on the temperature coefficients of the polarizations of more bromo compounds are available, the value of their atomic polarizations will have to remain an open question.

The fluoroethanes present an interesting group. Two of them, CF_3CF_3 and $CClF_2CClF_2$, should be non-polar; this fact gives $P_A = 6.5$ for C_2F_6 and $P_A = 14.2$ for $C_2Cl_2F_4$. If we use $P_A = 6.5$ for CH_3CF_3 and CH_3CClF_2, we obtain $\mu(CH_3CF_3) = 2.27$ and $\mu(CH_3CClF_2) = 2.13$. We can compare these figures with the results for the methanes as follows

$$(CH_3CF_3) = (CH_3C) + 3(CF)\cos 70° = 2.27$$
$$(CH_3CF_2Cl) = (CH_3C) + {}^1/_3(2CF + CCl) = 2.13$$

whence (CF) − (CCl) = 0.42, in agreement with the earlier figures. For CF_3CF_2Cl, we have $(P - P_E) = 13.2$, which is smaller than the corresponding figure for the non-polar $C_2F_4Cl_2$. But within the experimental error, we can set $P_A = 12.8$ for CF_3CF_2Cl, which gives it a moment of 0.14, in agreement with the other moments

$$(CH_3CF_3) - (CH_3CClF_2) = 0.14$$
$$(CF_3CClF_2) = 0.14$$

We could, in analogy with 1,1,2,2-tetrachloroethane, for which $\mu = 1.6$,[13] assume that $C_2Cl_2F_4$ had a finite moment, in which case the atomic polarizations for the fluorinated ethanes would be reduced from the values assumed here, and all moments would be correspondingly increased.

Finally, the compound $C_2H_2FCl_3$ will be considered. It was prepared by fluorination of $CHCl_2CHCl_2$ and one naturally would expect it to be $CHFClCHF_2$. However, the dipole moment agrees more closely with the structure CF_3CH_2Cl. If we use $P_E = 15.7$ and $P_A = 12.8$, we find $\mu(C_2H_2F_3Cl) = 1.64$. Then we have

$$(CF_3CH_2Cl) = (CF_3C) + {}^1/_3(2CH - CCl) = 1.64$$
$$(CF_3CH_3) = (CF_3C) + 3(CH)\cos 70° = 2.27$$

whence (CH) + (CCl) = 1.89, which agrees very closely with the value 1.85 used by Smyth and McAlpine for methyl chloride. The other isomer, CF_2ClCH_2F, gives (CH) + (CF) = 1.47, compared to the accepted value 1.81. The vapor density of the sample indicates a small amount of an impurity of higher molecular weight, but it hardly seems possible that the presence of an impurity could raise the moment from 0.1–0.2 expected for $CHFClCHF_2$ to the value observed. The only explanation which can be advanced on the basis of the present evidence is that rearrangement took place during fluorination.

Summary

The total polarization of a series of fluorine compounds has been determined by Schering bridge measurements on the gases. By making reasonable assumptions concerning the electronic and atomic polarizations, values for their dipole moments were obtained as follows: CF_4, 0.0; CF_3Cl, 0.47; CF_2Cl_2, 0.55; $CFCl_3$, 0.53; CHF_2Cl, 1.41; $CHFCl_2$, 1.34; CHF_2Br, 1.30; CF_2Br_2, 0.72; CF_3CF_3, 0.0; $CClF_2CClF_2$, 0.0; CH_3CF_3, 2.27; CH_3CClF_2, 2.13; CF_3CF_2Cl, 0.14; CF_3CH_2Cl, 1.64. These figures are in agreement with the theory of induction between dipole moments.

SCHENECTADY, N. Y. RECEIVED MAY 14, 1938

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[12] Morgan and Lowry, *J. Phys. Chem.*, **34**, 2385 (1930).

[13] Smyth, "Dielectric Constant and Molecular Structure," Chemical Catalog Co., New York, 1931, p. 201.