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The Dipole Moments of the Methyl and Ethyl Halides

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The dielectric constants of the vapors of the methyl and ethyl halides have been measured in order to obtain accurate values for their dipole moments. The increase in moment from the methyl to the ethyl halide accords with the previously advanced hypothesis of an inductive effect, but the change in the increase with change in the halogen involved points to the influence of an additional factor. The change in moment from compound to compound is compared with the change in the Raman frequency associated with the carbon-halogen bond.

BECAUSE of the importance of the dipole moments associated with the carbon-halogen bonds and because of interest in the effect of the carbon chain upon the moment of the molecule, it has seemed desirable to make accurate determinations of the moments of the methyl and ethyl fluorides, bromides and iodides in the vapor state, the chlorides having been previously so determined.¹ Moreover, results on the alkyl halides in solution gave abnormally high values for the atomic polarization, which suggested the possibility of a gradual increase in moment with rising temperature, a possibility requiring thorough investigation. Although the values reported by Mahanti² 2.00×10^{-18} for ethyl chloride and 2.03×10^{-18} for propyl chloride are in excellent agreement with the accurately determined values of Sanger and Fuchs, his value 2.00×10^{-18} for methyl chloride is considerably higher than the 1.86×10^{-18} found by both of these investigators. The similar identity which Mahanti reports in the cases of the methyl, ethyl and propyl bromides and the iodides is so different from the behavior found in solution³ that his moment values could not be regarded as a basis for discussion.

The dielectric constants were measured with the apparatus previously described,⁴ except that

the gold-palladium cell used by Zahn⁵ was employed in the measurements on ethyl fluoride and the iodides. As in earlier work,⁶ the polarization P was calculated from the dielectric constant ϵ and the molar volume V as $P = [(\epsilon - 1)/(\epsilon + 2)]V$, the polarization-pressure curve at each absolute temperature T being extrapolated to zero pressure to obtain a value for use in the Debye equation, $P = a + b/T$. The value of the atomic polarization was calculated as $P_A = a - P_E$, the difference between a , the total induced polarization, and P_E , the molar refraction extrapolated to infinite wave-length. The dipole moments were calculated from the values of b as $\mu = 0.01273 \times 10^{-18}(b^{\frac{1}{2}})$ and should be in error by no more than 0.01×10^{-18} .

PREPARATION AND PURIFICATION OF MATERIALS

Methyl fluoride

Methyl fluoride was prepared from potassium fluoride and potassium methyl sulfate by the method described by Bennett.⁷ Different fractions of the material, even the first and last, gave polarization values differing by less than the error of measurement.

Ethyl fluoride

261 grams of mercurous fluoride prepared according to Ruff⁸ and 207 grams of ethyl iodide, purified as described below, were allowed to react

¹ R. Sanger, *Helv. Phys. Acta* **3**, 161 (1930); *Phys. Zeits.* **32**, 20 (1931); O. Fuchs, *Zeits. f. Physik* **63**, 824 (1930).

² P. C. Mahanti, *Phys. Zeits.* **31**, 546 (1930).

³ C. P. Smyth, *Dielectric Constant and Molecular Structure*, p. 102, New York, The Chemical Catalog Co., Inc., 1931.

⁴ McAlpine and Smyth, *J. Am. Chem. Soc.* **55**, 453 (1933).

⁵ C. T. Zahn, *Phys. Rev.* **24**, 400 (1924).

⁶ Smyth and McAlpine, *J. Chem. Phys.* **1**, 190 (1933).

⁷ W. H. Bennett, *J. Am. Chem. Soc.* **51**, 377 (1929).

⁸ O. Ruff, *Die Chemie des Fluors*, p. 34, Berlin, Springer (1920).

under ordinary pressure in a vessel made of black iron pipe provided with suitable caps for the ends. The reaction vessel was maintained at about 70° , and the effluent gases were passed upward through a glass spiral surrounded by a toluene bath maintained at -35 to -30° in order to remove most of the ethyl iodide vapor carried along and then into a trap maintained at -78° , where the reaction product condensed. The 40 cc of liquid thus obtained was evaporated through long drying tubes of calcium chloride and phosphorus pentoxide and again condensed. This material was then given a series of fractionations between large traps, and the various fractions were tested for vapor pressure and polarization. The first fractions showed high vapor pressures because, apparently, of the presence of ethylene, but the later fractions, the last 5 cc having been discarded, had vapor pressures between 401.9 mm and 410.6 mm, corresponding to a boiling point range of less than 0.5° . The polarization values determined for three fractions within these limits showed no detectable differences. Two 5 cc fractions differing by 2.1 mm in vapor pressure were combined and measured to obtain the following vapor pressure values: -50.0° , 406.1 mm; -40.0° , 687.9 mm; -37.8° , 760 mm. The boiling point -37.8° thus obtained is considerably lower than the value -32° given by *International Critical Tables*, but it is believed that so large a discrepancy cannot arise from the small quantities of impurities presumably remaining in the material here measured, which is judged to be of satisfactory purity. Small quantities of the material obtained in previous preparations of inadequate yield had vapor pressures approximately equal to the values found for this large preparation.

Methyl bromide

Kahlbaum's material was passed through spiral wash bottles containing water and concentrated sulfuric acid, then through drying tubes filled with calcium chloride and phosphorus pentoxide, and finally was condensed in a trap. The polarizations of the first and last fractions of the material were identical within the limits of experimental error.

Ethyl bromide

Merck's C.P. material was shaken three times with concentrated sulfuric acid, once with water, once with 10 percent sodium carbonate solution, then three times with water. It was dried over two separate portions of calcium chloride, then over phosphorus pentoxide, and was finally fractionally distilled; b.p., 37.9 – 38.1° ; n_D^{20} , 1.42443.

Methyl iodide

Merck's methyl iodide was shaken several times with portions of water, dried, first over calcium chloride, then over phosphorus pentoxide, and finally fractionally distilled; b.p., 42.6° ; n_D^{20} , 1.53067.

Ethyl iodide

Ethyl iodide from the Sterling Products Company was shaken with mercury until the yellow color was gone, filtered, shaken repeatedly with fresh portions of water, dried, first over calcium chloride then over phosphorus pentoxide, and fractionally distilled; b.p., 72.4 – 72.6° ; n_D^{20} , 1.51336.

EXPERIMENTAL RESULTS

As a check upon the accuracy of the apparatus seven runs were made with air at 28.1°C and at pressures between 925 and 1122 mm. When reduced to 0° and 760 mm, they gave a mean value 581 for $(\epsilon-1)\times 10^6$, identical with that found in the earlier measurements.⁴ After the gold-palladium cell had been substituted for the copper cell and a larger fixed condenser introduced into the apparatus, ethyl bromide vapor was run at 412.2°K for comparison with the value obtained with the copper cell. The mean of seven determinations of the polarization, 81.96, was half a percent lower than the value 82.38 previously obtained with the copper cell, a difference so small as to affect the moment value by no more than 0.005×10^{-18} .

The error in the polarization values caused by the use of the ideal gas law in their calculation is eliminated by the extrapolation to zero pressure to obtain the values of P_0 given in Table I. The polarization-pressure curve at these pressures is a straight line, usually obtained by plotting six or eight polarization values at each temperature

TABLE I. Polarization values.

<i>T</i> , °K	<i>P</i> ₅₀₀	<i>P</i> ₀	<i>T</i> , °K	<i>P</i> ₅₀₀	<i>P</i> ₀
Methyl fluoride			Ethyl bromide		
224.0	99.84	98.20	303.4	106.0	104.2
237.4	95.14	93.90	306.6	105.2	103.5
252.4	89.04	87.94	352.3	93.64	92.70
272.7	83.66	83.12	394.7	86.04	84.90
301.2	76.74	76.40	441.4	78.4	78.4
334.1	69.86	69.68	Methyl iodide		
380.3	62.38	62.26	304.7	73.80	71.82
414.3	57.70	57.60	313.4	71.95	70.15
451.0	53.66	53.60	345.9		65.3
498.1	49.40	49.37	398.6		59.4
Ethyl fluoride			446.7		55.5
236.2	108.5	107.3	494.4		51.8
298.4	88.88	88.60	Ethyl iodide		
328.8	81.62	81.34	348.3	92.05	89.95
372.5	73.37	73.26	411.4	81.00	79.40
422.0	65.90	65.90	434.3	78.44	77.15
480.8	59.26	59.26	463.2	74.60	74.00
534.6	54.14	54.14	Methyl bromide		
Methyl bromide			306.2	80.98	79.60
			309.1	80.18	78.85
			330.8	75.57	74.40
			368.0	69.16	68.40
			405.9	64.12	63.85

against the pressures at which they are determined. The course of each curve is shown by giving as P_{500} the polarization value at 500 mm, sometimes obtained by extrapolation. In the case of methyl iodide, the values of P_{500} are omitted at the higher temperatures where the slopes of the curves are uncertain. As the temperature rises, the decreasing difference between P_{500} and P_0 shows the decreasing deviation of the vapor from ideal behavior, the difference often being undetectable at the highest temperatures measured. The P_0 values are used to calculate by the method of least squares the constants given in Table II. The values of a and μ for methyl and ethyl chloride are the means of those obtained by Sanger¹ and Fuchs.¹ The last column of Table II gives the increase in moment from the methyl to the corresponding ethyl halide.

DISCUSSION OF RESULTS

The atomic polarizations of these substances, with the exception of ethyl fluoride, have been included in the discussion of the problem of atomic polarization in an earlier paper,⁹ where

TABLE II. Constants of methyl and ethyl halides.

	<i>a</i>	<i>P</i> _E	<i>P</i> _A	<i>b</i>	$\mu \times 10^{18}$	(C ₂ H ₅ -CH ₃) $\times 10^{18}$
CH ₃ F	8.95	6.6	2.4	20170	1.808	
C ₂ H ₅ F	14.04	11.1	2.9	22760	1.92	0.11
CH ₃ Cl	13.6 ¹	12.0	1.6		1.86 ¹	
C ₂ H ₅ Cl	19.3 ¹	16.6	2.7		2.03 ¹	.17
CH ₃ Br	15.40	14.2	1.2	19580	1.78	
C ₂ H ₅ Br	21.49	18.6	2.9	25080	2.02	.24
CH ₃ I	20.22	18.5	1.7	15650	1.59	
C ₂ H ₅ I	25.71	23.3	2.4	22290	1.90	.31

⁹ C. P. Smyth, J. Chem. Phys. **1**, 247 (1933).

they served to prove the incorrectness of some abnormally high values obtained from measurements on liquids. A revision of the data has altered a number of the values somewhat, increasing the accuracy sufficiently to make apparent an increase in P_A from the methyl to the ethyl compound in accordance with the general tendency previously observed¹⁰ for an increase in P_A with increase in the number of atomic nuclei or groups in the molecule.

The decrease in moment from the chloride to the iodide is much less pronounced than in the case of the hydrogen halides, for which the values are 1.03, 0.78, and 0.38×10^{-18} for HCl, HBr and HI, respectively.⁵ This rapid decrease in the hydrogen halides, in spite of the increased nuclear separation, is undoubtedly due to the increased shift of negative charge toward the positive because of the increasing polarizability of the halogen.¹¹ As the positive charges of the methyl group are not as near to the negative charges of the halogen as is the proton in the hydrogen halides, the displacement of the negative charges should be smaller in the methyl halides so that the moments should fall off less rapidly with increasing halogen polarizability. A rough value 0.8×10^{-18} may be calculated for HF by assuming the ratio of the HF moment to the observed HCl moment to be equal to the ratio of the moment values calculated by Kirkwood¹² for these two molecules. Although this value may be too approximate to be significant, it is interesting to note that it is lower than the HCl moment, while the values for methyl and ethyl fluoride are also slightly lower than those for the corresponding chlorides.

It is obvious that there are, at least, two opposing factors determining the moments. Increase in the carbon-halogen distance should tend to increase the moment, while increase in the halogen polarizability should decrease it. It appears that the 0.35Å increase in the distance between the carbon and halogen nuclei from the fluoride to the chloride more than compensates for the increase in halogen polarizability, while the effects of the smaller increases in nuclear separation, 0.15Å from the chloride to the

¹⁰ C. P. Smyth, J. Am. Chem. Soc. **51**, 2051 (1929).¹¹ C. P. Smyth, Phil. Mag. **47**, 530 (1924).¹² J. G. Kirkwood, Phys. Zeits. **33**, 259 (1932).

bromide and 0.19A from the bromide to the iodide, are overbalanced by the greater electronic shifts permitted by greater polarizability. The decrease in moment produced by changing from one halogen to the next larger increases by $0.12 \pm 0.01 \times 10^{-18}$ for each change in going down the series from fluoride to iodide in both the methyl and the ethyl halides. Thus, the difference between $\text{CH}_3\text{F} - \text{CH}_3\text{Cl} = -0.05$ and $\text{CH}_3\text{Cl} - \text{CH}_3\text{Br} = 0.08$ is -0.13 and the difference between $\text{CH}_3\text{Cl} - \text{CH}_3\text{Br} = 0.08$ and $\text{CH}_3\text{Br} - \text{CH}_3\text{I} = 0.19$ is -0.11 . The difference between the corresponding methyl and ethyl halides increases by 0.07×10^{-18} with each change from one halogen to the next larger.

It was shown years ago^{3, 13} that the greater moment of an ethyl halide as compared to a methyl was presumably due to the moment induced in the second carbon by the principal dipole in the carbon-halogen bond. Beyond this second carbon the effect of induction is practically negligible as far as the moment is concerned since higher primary alkyl halides were found to be practically indistinguishable in moment from the ethyl compound, a result confirmed in the case of the chlorides by Sanger's¹ value 2.04×10^{-18} for propyl chloride vapor and a value 2.04×10^{-18} for butyl chloride vapor shortly to be published from this laboratory. However, a secondary alkyl halide has been found to have a larger moment than a primary, while a tertiary has one still larger, indicating that, when additional carbons are brought within the effective field of the principal carbon-halogen dipole, measurable moments are induced upon them. A branch farther along the chain, as in an isobutyl halide, does not increase the moment, the field due to the principal dipole being apparently insufficient to induce a detectable moment in these more remote carbons.

The precise location of the principal dipole in the carbon-halogen bond is not known, but it has seemed reasonable to locate it $7/8$ of the distance from the carbon nucleus to the halogen nucleus¹⁴ and calculations of induced moments based on this assumption have given good agreement with observed values.⁶ The distance of the principal

dipole from the second carbon of the ethyl halide should increase with increasing size of the halogen and its inductive effect upon the charges of this carbon should, therefore, decrease unless the principal dipole itself increases. Although a rough calculation of this principal dipole moment gave 0.91 and 1.15×10^{-18} for methyl fluoride and methyl chloride,⁶ a similar calculation gives 1.18 for the bromide and 1.14×10^{-18} for the iodide. The increasing methyl-ethyl difference with increasing halogen size is, therefore, contrary to what would be predicted on the basis of inductive effect and indicates that some other factor must play a part.

It is interesting to note qualitative analogies and differences between the alkyl halide moments and the Raman frequencies associated with the carbon-halogen bonds.¹⁵ The frequency which probably corresponds to a longitudinal vibration in the carbon-halogen line drops from the methyl to the ethyl and remains constant as the carbon chain is lengthened from two to five atoms just as the moment remains constant in the case of the chlorides after a rise from methyl to ethyl. A secondary chloride shows a further decrease in frequency and increase in moment and a tertiary chloride a still further decrease in frequency and increase in moment. Branching of the chain at the second carbon increases the Raman frequency, but, as far as can be judged from measurements on the liquid, leaves the dipole moment identical with that of the normal compound. Branching of the chain at the third carbon or beyond in the halides leaves both the Raman frequency and the moment unaffected. Generally, in these compounds, decrease in frequency appears to accompany increase in moment. However, the decrease in frequency from methyl to ethyl becomes smaller with increasing halogen size, in part, at least, a mere mass effect, while the increase in moment becomes greater.

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¹³ C. P. Smyth and H. E. Rogers, *J. Am. Chem. Soc.* **52**, 2227 (1930); C. P. Smyth and R. W. Dornte, *ibid.* **53**, 545 (1931).

¹⁴ L. Meyer, *Zeits. f. physik. Chemie* **B8**, 27 (1930).

¹⁵ W. D. Harkins and H. F. Bowers, *J. Am. Chem. Soc.* **53**, 2425 (1931); W. D. Harkins and R. R. Hann, *ibid.* **54**, 3920 (1932).