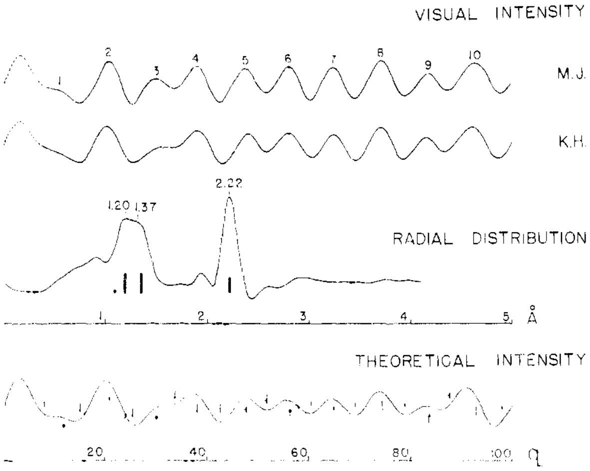

Fig. 1.—Electron diffraction curves for formyl fluoride. The theoretical intensity curve is for C–F/C=O = 1.133 and ∠F—C=O = 121°.

The limits of error for C–F/C=O and ∠O–C–F are surprisingly small compared to the values ±0.009 and ±1.7° first derived for these parameters by the correlation procedure. It appears that one important reason for this difference is the inclusion of the measurements of positions of features in the least squares equations. In ordinary practice of the correlation procedure the contribution of such measurements is often neglected in the determination of shape parameters. A least squares determination of the shape parameters for formyl fluoride omitting the measurement of positions of features leads to the results C–F/C=O = 1.135 ± 0.006 and ∠O–C–F = 121.5 ± 1.3°.

Discussion

Our C–F and C=O bond lengths for formyl fluoride are consistent with the corresponding lengths in many other molecules in that each bond is somewhat shortened relative to its length in the relevant methane where only one substituent is present (CH_3F, CH_2O). Comparison with the values reported for acetyl fluoride (1.37, 1.16 Å.)[10] is not simple, however, the substitution of methyl for hydrogen having opposite effects on C–F and C=O whereas the most natural expectation would be of lengthening for both. All in all, it seems best that further discussion should await a wider survey of the facts than is here feasible.

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[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

The Electric Moments of Some Interhalogen Compounds[1]

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The electric moments of bromine trifluoride, chlorine trifluoride and iodine pentafluoride have been measured in the vapor phase by the refractivity method. A planar T-configuration for bromine trifluoride, similar to that now established for chlorine trifluoride, accounts satisfactorily for the dipole moment of the molecule. The large electric moment of iodine pentafluoride excludes the trigonal bypyramidal and pentagonal planar structures. It is in satisfactory agreement with a distorted octahedral arrangement in which the iodine atom is probably below the plane of the four fluorine atoms on the side opposite the fifth fluorine atom, and the unshared pair is in the sixth position.

Introduction

The electric moments of chlorine monofluoride, bromine monofluoride and chlorine trifluoride have been found by microwave methods[2] but the only halogen fluoride studied by conventional radiofrequency techniques is bromine pentafluoride.[3] The dielectric constants and electric dipole moments of bromine trifluoride, chlorine trifluoride and iodine pentafluoride in the vapor state have, therefore, been measured at radio-frequencies. The results are reported here along with some conclusions concerning the structures of the molecules.

Experimental

Materials.—Bromine trifluoride and chlorine trifluoride (Harshaw Chemical Co.) were purified by several distillations in a Monel apparatus. The middle fraction of the final distillation was used in each case for the measurements. Iodine pentafluoride was part of a sample purified by distillation through a packed column[4]; the mole per cent. impurity indicated by freezing point lowering measurements was about 0.02 mole %.

Apparatus.—Dielectric constants were measured by the heterodyne-beat method. The fixed oscillator was crystal-controlled at 500 kc. and the variable-frequency-oscillator was of the negative-transconductance type described by Chien.[5] The beat frequency was compared with a fixed-frequency 400-cycle reference using an oscilloscope; in this way locking-in of the oscillators was prevented.

Capacitance was measured by the substitution method using a General Radio type 722-N precision capacitor (1100 $\mu\mu$f.). Introduction of the gas into the measuring cell increased the capacitance in the tank-circuit of the variable-frequency oscillator; the precision capacitor was then adjusted to restore the original beat frequency. To produce a suitably large change of scale reading on the precision capacitor from the very small capacitance changes obtained, and to have a nearly linear relationship between these, auxiliary capacitors were employed in a network arrangement. The precision capacitor and a Type 380-M General Radio mica decade (0.01 to 0.001 mf.), were placed in parallel and this combination was then used in series with a small variable air capacitor (175 $\mu\mu$f.). The measuring cell was then arranged in parallel with the above system of three capacitors in the tank circuit of the oscillator. The ranges were adjusted so that 10,000 dial units on the precision ca-

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(1) Physical Properties of the Halogen Fluorides. IV. For preceding article of this series see M. T. Rogers, M. B. Panish and J. L. Speirs, THIS JOURNAL, **77**, 5292 (1955).

(2) "Table of Electric Dipole Moments of Substances in the Gaseous State," Bureau of Standards Circular 537, Washington, D. C., 1953.

(3) M. T. Rogers, R. D. Pruett, H. B. Thompson and J. L. Speirs, unpublished results.

(4) M. T. Rogers, J. L. Speirs, H. B. Thompson and M. B. Panish, THIS JOURNAL, **76**, 4843 (1954).

(5) J. Chien, *J. Chem. Educ.*, **24**, 494 (1947).

pacitor was equivalent to a change of about 3.7 $\mu\mu$f. in the measuring cell. An additional advantage of this arrangement is that one side of both the precision capacitor and the mica decade are grounded.

The precision capacitor (and associated network) was calibrated in place at the frequency of measurement by use of a primary standard similar to that designed by Conner.[6] In this instrument a central rod, with its opposite ends inserted in cylinders of different diameters, can be moved along its axis; the capacitance change per inch of travel was calculated from the geometry of the precisely-machined capacitor. To improve the precision, only the central portion of the scale was used. This device was substituted for the dielectric cell using the same coaxial leads; a calibration curve was then obtained which enabled readings on the General Radio precision capacitor to be converted to micromicrofarads.

The dielectric cell was a very rigid one with outer and inner cylinders machined from Monel stock and separated by Teflon insulators. Inner cylinders of different diameters could be substituted; it was found necessary to increase the spacing between the cylinders to 0.087″ for this investigation in order to reduce errors resulting from adsorption.

Pressures were measured to ±1 mm. by use of a Monel Bourdon gage which was calibrated against a mercury manometer at each temperature. The Bourdon tube and the associated metal vacuum line were electrically heated to the temperature of the cell. The temperature of the cell was controlled to ±0.05° at each temperature by a large regulated constant-temperature bath. A thermistor was the temperature-sensitive element and the heater current was controlled by a saturable reactor.[7]

Method.—The cell was calibrated with purified samples of ammonia and carbon dioxide. The replaceable capacitance (111 $\mu\mu$f.) was found using the reported dielectric constants of these substances.[2,8]

The capacitance of the cell was then measured at several pressures when filled with the vapor of a given substance at a fixed temperature. The values so obtained were plotted graphically *versus* pressure and the capacitance change ΔC, from vacuum to one atmosphere pressure, found. Deviations from the ideal gas law and errors due to adsorption were eliminated to some extent by working only at those pressures and temperatures for which the graph was nearly a straight line. From ΔC and the known replaceable capacitance of the cell the dielectric constant of the gas at one atmosphere pressure was calculated. Measurements were repeated at several temperatures for each substance and the observed dielectric constants are shown in Table I along with the molar polarizations calculated from the Debye equation. Molar volumes were computed from the ideal gas equation or Berthelot's equation (chlorine trifluoride and ammonia).

Only a narrow temperature range was available in which bromine trifluoride and iodine pentafluoride could be studied since adsorption and deviations from the ideal gas law became important at higher pressures and lower temperatures than those reported in Table I. A precise value of the dipole moment, therefore, could not be found by the temperature method. The molar refractions MR_D are known[9] and to these were added estimated values of the atomic polarization P_A. The resulting distortion polarizations P_D were subtracted from the observed total molar polarization values P_M to obtain the orientation polarizations. The dipole moment μ was calculated by use of the equation

$$\mu = 0.0128\sqrt{P_M - P_A - MR_D}$$

The atomic polarizations of chlorine trifluoride and bromine pentafluoride were estimated from the observed molar refractions[8] (10.34 and 15.48) and distortion polarizations[3,10] (15.94 and 18.98); the atomic polarizations of bromine trifluoride and iodine pentafluoride were assumed to be the same as those of chlorine trifluoride (5.5) and bromine pentafluoride (3.5), respectively. The molar refractions, atomic polarizations and average dipole moments (from molar polarizations at three or four temperatures) are shown in Table II. The dipole moments listed have a probable error of about ±0.12 debye.

TABLE I

DIELECTRIC CONSTANTS AND MOLAR POLARIZATIONS OF SOME HALOGEN FLUORIDES AT VARIOUS TEMPERATURES

T, °K.	$(\epsilon - 1) \times 10^6$	P_M (cc./mole)
	Iodine pentafluoride	
392.7	9108	97.6
408.1	8468	94.3
423.5	7973	92.2
446.0	7135	86.9
	Bromine trifluoride	
415.5	3748	42.6
424.7	3189	37.0
448.2	2964	36.3
	Chlorine trifluoride	
319.3	2825	24.2
351.8	2490	23.6
375.8	2293	23.3
413.3	1929	21.7

TABLE II

MOLAR REFRACTIONS, ATOMIC POLARIZATIONS AND DIPOLE MOMENTS OF SOME HALOGEN FLUORIDES

Compound	MR_D[a]	P_A,[b] cc./mole	μ[c]
Iodine pentafluoride	19.17	3.5	2.18
Bromine trifluoride	12.92	5.5	1.19
Chlorine trifluoride	10.34	5.5	0.65

[a] M. T. Rogers and J. G. Malik, unpublished results. [b] Estimated (see text). [c] Average of values found at three or four different temperatures.

Results

The electric moment of chlorine trifluoride at radio-frequencies which is reported here (0.65) agrees within our experimental error with the more precise value 0.554 found at microwave frequencies.[10] Since our data do not permit a precise determination of the electric moment by the temperature method the total polarizations at the four temperatures studied have been combined with the distortion polarization reported by Magnuson[10] (15.94 cc./mole) to obtain the value in Table II. Chlorine trifluoride is known to have a planar T-configuration[11] with the central Cl–F bond shorter than the other two by 0.1 Å. and angles F–Cl–F about 87°. The electric moment of the molecule is nearly equal to the bond moment of the central bond which is, therefore, about 0.3 *D* smaller than the Cl–F bond moment in chlorine monofluoride[2] (0.88 *D*). If the shortening of this bond arises from some double bond character the smaller bond moment would be reasonable.

The electric moment of bromine trifluoride (1.19) is slightly smaller than that of bromine monofluoride[2] (1.29). The analogy with chlorine trifluoride is close enough to suggest that the structures are similar and that bromine trifluoride also has a planar T-configuration with the central bond different from the other two. If the angles Br–F–Br are 87° as in chlorine trifluoride the moment of the central Br–F bond in bromine tri-

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(8) A. Van Itterbeek and K. de Clippeleir, *Physica*, **14**, 349 (1948).

(9) M. T. Rogers and J. G. Malik, unpublished results.

(10) D. W. Magnuson, *J. Chem. Phys.*, **20**, 229 (1952).

(11) D. F. Smith, *ibid.*, **21**, 609 (1953).

fluoride would be about 0.25 *D* lower than the Br–F moment in bromine monofluoride.

The high value of the electric moment of iodine pentafluoride (2.18) excludes the trigonal bipyramidal or pentagonal planar configuration for the molecule. A distorted octahedral arrangement with the iodine atom below the plane of the four fluorine atoms, on the side opposite the fifth fluorine atom, (giving four angles F–I–F of about 85°) was proposed on the basis of an electron diffraction investigation.[12] This structure would account satisfactorily for the dipole moment. The I–F bond moment should be about 1.6 (by analogy with the known ClF and BrF moments) and, if the bond moments in iodine pentafluoride were all equal, this would lead to the observed moment for the molecule. However, the nuclear magnetic resonance spectrum[13] indicates that one bond differs from the other four so it might be expected by analogy with chlorine trifluoride that the unique I-F bond moment would be smaller than the other four. While a pentagonal pyramidal configuration would also account for the dipole moment it appears to be ruled out by the infrared spectrum,[14] and it is certainly eliminated by the nuclear magnetic resonance data.

The interpretation of the electric moments of the halogen fluorides is particularly difficult. The σ-bonds in these molecules might be considered to be dsp^3 hybrids in the trifluorides and d^2sp^3 hybrids in the pentafluorides with the unshared electron pairs sterically active. The tendency of unshared pairs to occupy more space than expected from symmetry[15] would then account for the angles F–X–F being 85–87° rather than right angles. It has been shown theoretically that when d-orbitals are used the contribution of the lone pairs of electrons to the dipole moment of a molecule is very sensitive to the amount of d-character in the bonds and may be quite large.[16] Since additional orbitals are available for π-bond formation in these molecules, and the bonds are known not to be equivalent, this factor may also be of importance. It is therefore difficult to even predict theoretically the direction of the total moment. Since the homopolar dipole[16] and the electronegativity differences both favor the conventional direction of the bond moment we have assumed this in the above discussion. A detailed analysis of the electron distribution in these molecules, however, will require in addition data obtained by other techniques.

Acknowledgment.—The authors are grateful to the Atomic Energy Commission for support of this work through Contract AT(11-1)-151.

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Thermal Decomposition of Sulfides

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The thermal decomposition of methyl benzyl sulfide has been investigated, in a flow system, in the presence of a large excess of toluene as a carrier gas and a free-radical trap. The decomposition is a homogeneous, first-order free-radical process with an activation energy of 51 ± 2 kcal. mole^{-1}, which has been identified with the dissociation energy of the $C_6H_5 \cdot CH_2–S \cdot CH_3$ bond. Preliminary results show that dimethyl sulfide decomposes by a free radical process and dimethyl disulfide by a molecular rearrangement.

Introduction

From the results of the recent kinetic study of the thermal decomposition of benzyl, methyl and ethyl mercaptans in a stream of toluene, Sehon and Darwent[4] derived the C–S bond dissociation energies and proposed a value of about 32 kcal./mole for the heat of formation of the SH radical.

Those studies have been extended, in the present investigation, to benzyl methyl sulfide, dimethyl sulfide and dimethyl disulfide in an attempt to determine the relevant C–S bond dissociation energy and the heat of formation of the SCH_3 radical.

Materials.—The toluene used was the Phillips Petroleum Company's research grade product; dimethyl sulfide and dimethyl disulfide were commercial Eastman Kodak samples and were used without further purification. Methyl benzyl sulfide was prepared by Eastern Chemicals and was purified by distillation under reduced pressure (12 mm.) through a Stedman fractionation column, only the middle fraction being used for pyrolysis.

Experimental

The thermal decomposition of the sulfides was studied in a flow system in the presence of excess toluene using the technique developed by Szwarc.[5] The apparatus used was essentially the same as that described previously.[4] Minor alterations were made in the method of separating and analyzing the products of reaction. The products together with undecomposed sulfide and toluene were made to flow, after passage through the furnace, through one trap kept at 0° and two traps at −195°. Most of the dibenzyl produced crystallized out in the trap at 0°, the other condensable products, toluene and undecomposed sulfide, being removed

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