

In Fig. 3 are plotted the melting points of the compounds as a function of the empirical ionic radii for the oxides.¹⁰ The melting points lie on a smooth curve with the exception of $(C_5H_5)_3La$; unlike the melting points of the halides there is no reversal in the region of terbium with a subsequent increase in melting point in going towards Lu, although there is a change in the slope of the curve.

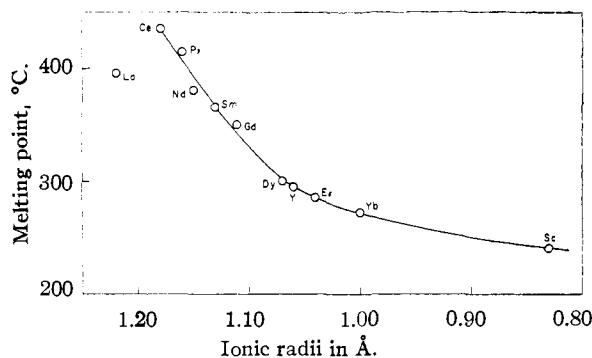
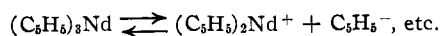


Fig. 3.—Melting points of the $(C_5H_5)_3M$ compounds vs. ionic radii of M^{3+} .

Discussion

The chemical and physical properties of the $(C_5H_5)_3M$ compounds clearly indicate their ionic nature. Thus while the dissociation, *e.g.*



is very small, perhaps attributable in part to a low tendency of the anion to solvate, the instantaneous liberation of cyclopentadiene with water or acids, and the instantaneous quantitative reaction with ferrous chloride to form ferrocene, show that the above type of equilibria are labile, and that agents attacking the cyclopentadienide ion will rapidly displace the equilibrium. The reactivity of the compounds toward maleic anhydride, aldehydes, ketones and halogenated solvents is due to this fact also.

The ionic nature of the compounds is also shown

(10) T. Moeller, "Inorganic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1952, p. 147.

by properties dependent upon the metal atom. Thus the magnetic susceptibility values are very close to those for the rare earth ions in other compounds and there is little doubt that the metal to ring bonds in $(C_5H_5)_3M$ compounds are electrostatic in nature. The similarity of the absorption spectra of the $(C_5H_5)_3M$ compounds in tetrahydrofuran to those of the ions in aqueous solution is also in agreement with the ionic nature of the bonding; in the cyclopentadienides the bands are sharper and somewhat shifted to longer wave lengths.

In the absence of X-ray data, little can be said concerning the structure of the cyclopentadienides in the crystal or as the free molecules. Since the metal to ring bonds are electrostatic the $C_5H_5^-$ ions may be expected to lie with their centers at the vertices of an equilateral triangle at whose center is placed the metal ion; with such an arrangement the electrostatic energy would be at a minimum. The comparatively low melting points and ready volatilities suggest that the compounds exist, even in the crystals, as ionically bonded molecules. It is noteworthy that methyl substitution in the anion lowers the melting point for the neodymium cyclopentadienide by 215° ¹¹; ethylcyclopentadienides may be expected to melt at even lower temperatures and since steric hindrance may be expected with bulky substituents on the $C_5H_5^-$ ion, even greater differences may be found in melting points and volatilities over the range of the rare earth elements than occur with the $(C_5H_5)_3M$ compounds.

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(11) L. T. Reynolds and G. Wilkinson (unpublished work).

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Bromine Pentafluoride. The Electric Dipole Moment in the Vapor State and the Dielectric Constant of the Liquid¹

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The electric moment of bromine pentafluoride, determined from the dielectric constant of the vapor at several temperatures, is $1.51 \pm 0.10 D$. This value is consistent with a square prismatic structure for the molecule and excludes the trigonal bipyramidal and pentagonal planar configurations. The dielectric constant of the liquid in the range -12 to 25° may be represented by the equation $\epsilon = 8.20 - 0.0177 t$. This is close to the value calculated theoretically from the gas dipole moment and indicates that bromine pentafluoride is not an associated liquid (in the conventional sense).

Introduction

Since the structure of bromine pentafluoride is not known we have measured the electric moment in the vapor state to provide information concerning the structure. A comparison of the dielectric

constants of liquid chlorine trifluoride and iodine pentafluoride with the values calculated theoretically seemed to indicate that these are associated liquids.² This study has been extended to bromine pentafluoride by measurement of its dielectric constant over a range of temperature.

(1) Physical properties of the halogen fluorides V. For preceding article of this series see M. T. Rogers, J. L. Speirs and M. B. Panish, THIS JOURNAL, **77**, 5280 (1955).

(2) M. T. Rogers, H. B. Thompson and J. L. Speirs, *ibid.*, **76**, 4841 (1954).

Experimental

Dielectric Constant of Liquids.—The dielectric constant of the liquid was measured using a General Radio Twin-T impedance bridge. The sample was contained in a special cell, constructed of Nickel and Teflon, with a replaceable capacitance of 10.32 $\mu\mu$ farads. The apparatus, technique and method of calculation have been described.² The data of Table I may be represented by the equation

$$\epsilon = 8.20 - 0.0117t$$

to within $\pm 0.5\%$.

TABLE I

THE DIELECTRIC CONSTANT OF LIQUID BROMINE PENTAFLUORIDE AT VARIOUS TEMPERATURES

Temp.	24.5	14.5	0.2	-11.7
ϵ	7.91	8.02	8.21	8.33

Dipole Moment in the Vapor State.—The dielectric constant of the vapor was measured at several temperatures by the heterodyne-beat method. A special cell, constructed of Monel and Teflon, was used for these measurements; it has a replaceable capacitance of 133 $\mu\mu$ farads and was calibrated with ammonia and carbon dioxide. The cell temperature was regulated by a large constant-temperature bath. The pressure of the bromine pentafluoride vapor was measured by use of a Bourdon gage which was maintained at a temperature above that of the cell. The apparatus, technique and calculations have been outlined.³ The results are shown in Table II.

TABLE II

DIELECTRIC CONSTANTS AND MOLAR POLARIZATIONS OF BROMINE PENTAFLUORIDE VAPOR AT VARIOUS TEMPERATURES

$$P_D = 21.8 \text{ cc./mole}, \mu = 1.51 D.$$

Temp., °K.	ϵ	P , cc./mole
345.6	1.006320	59.6
362.6	1.005824	57.7
374.9	1.005525	56.6
388.9	1.005180	55.0
402.4	1.004910	54.0
417.2	1.004603	52.5
430.8	1.004378	51.5

Materials.—The bromine pentafluoride was part of a lot which had been fractionated in a Monel-packed Fluoroethene column and had been stored in Fluoroethene vessels. All manipulations were carried out in a nickel or Fluoroethene system. The impurity content, as indicated by an analysis of the freezing curve, was less than 0.5 mole %.⁴

Results

The molar polarizations of bromine pentafluoride at various temperatures are listed in Table II along with the observed dielectric constants of the gas (reduced to one atmosphere pressure). These values were plotted graphically *versus* the reciprocal of the absolute temperature and the distortion polarization was taken as the intercept at infinite temperature. The slope was found by the method of least squares and the dipole moment (1.51D) computed from this by use of the usual equations. The molar volume at each temperature was calculated by the ideal gas law. The electric moment is assigned a probable error of $\pm 0.10 D$ from an analysis of the errors in the present measurements.⁵

The electric moment observed for bromine penta-

(3) M. T. Rogers, R. D. Pruett and J. L. Speirs, *THIS JOURNAL*, **77**, 5280 (1955).

(4) M. T. Rogers and J. L. Speirs, unpublished results.

(5) R. D. Pruett, Doctoral Thesis, Michigan State College, 1954.

fluoride in the vapor state is slightly higher than that reported for bromine monofluoride⁶ (1.29 D). This shows that the structure is not trigonal bipyramidal or pentagonal planar; it is also evidence against a square pyramidal arrangement with the bromine appreciably above the base of the pyramid. If the Br-F bond moment is assumed to be the same as in bromine monofluoride, then the observed moment is accounted for by the square pyramidal configuration with the bromine atom slightly below the plane of the four fluorine atoms (angles F-Br-F about 88°). If the Br-F bond moment is lower than in bromine monofluoride, as is suggested by a comparison of the moments ClF⁶ (0.88) and ClF₃⁶ (0.54), the argument would be similar but the angles F-Br-F would be lower than 88°. Although a pentagonal pyramidal configuration could account for the electric moment it is ruled out by the nuclear resonance spectrum which indicates that one fluorine atom is in a different environment from the other four.⁷ Uncertainty as to the magnitude of the lone-pair moment, the homopolar dipole term⁸ and the orbitals used in σ - and π -bond formation, makes any detailed interpretation of the total moment difficult.

The dielectric constant of the liquid (7.90 D at 25°) may be compared with the value calculated theoretically for a liquid made up of molecules with the observed gas dipole moment. A comparison of the observed and the theoretical dielectric constants has been made by computing the correlation factor g using the expression

$$\epsilon - 1 = \frac{4\pi N}{3kTV} \left(\frac{3\epsilon}{2\epsilon + 1} \right) \mu^2 g + (\epsilon + 2) \left(\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} \right)$$

derived theoretically by Harris and Alder.⁹ The moment μ in the absence of the field was calculated from the moment of a free gas molecule by the equation

$$\mu = \mu_0 \left(\frac{\epsilon_\infty + 2}{3} \right) \left(\frac{2\epsilon + 1}{2\epsilon + \epsilon_\infty} \right)$$

The factor g represents the hindering effect of a molecule on its neighbors; positive or negative deviations of g from unity indicate co- or contra-association,¹⁰ respectively, of the molecules in the liquid.

The value $g = 0.95$ for bromine pentafluoride obtained by use of the above equations indicates that it is not appreciably associated in the liquid state. Iodine pentafluoride ($g = 1.50$),¹¹ on the other hand, shows a large positive deviation from unity indicating a considerable degree of co-association in the liquid phase.

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(6) "Table of Dielectric Constants and Electric Dipole Moments of Substances in the Gaseous State," Circular 537, National Bureau of Standards, Washington, D. C., 1953.

(7) H. S. Gutowsky, D. W. McCall and C. P. Slichter, *J. Chem. Phys.*, **21**, 279 (1953).

(8) C. A. Coulson, "Valence," Oxford University Press, 1952, p. 146.

(9) F. E. Harris and B. J. Alder, *J. Chem. Phys.*, **21**, 1031 (1953).

(10) J. N. Wilson, *Chem. Revs.*, **25**, 377 (1939).

(11) M. T. Rogers, unpublished calculation.