The Measurement of the Dielectric Constants of Vapors and the Polarizations of Trimethylaluminum, Dimethylaluminum Chloride and Methylaluminum Dichloride

R. H. Wiswall Jr. and C. P. Smyth

The Measurement of the Dielectric Constants of Vapors and the Polarizations of Trimethylaluminum, Dimethylaluminum Chloride and Methylaluminum Dichloride

R. H. WISWALL, JR. AND C. P. SMYTH

Frick Chemical Laboratory, Princeton University, Princeton, New Jersey

(Received January 9, 1941)

Modifications of an apparatus for the measurement of the dielectric constants of vapors are described. The apparatus has been used to determine the dielectric constants of the vapors of trimethylaluminum and dimethylaluminum chloride over a range of temperature and pressure, and methylaluminum dichloride has been measured in solution with another apparatus. The accurate calculation of the dipole moments of the molecules is prevented by strong molecular association. The data indicate a strong probability that the single trimethylaluminum molecule has a pyramidal structure and that the aluminum-carbon bond is predominantly covalent.

THE dipole moments of trimethylaluminum, dimethylaluminum chloride and methylaluminum dichloride would be of considerable interest not only because of the light which they might throw upon the molecular structures of these compounds but also as a means of obtaining moment values for the aluminum bonds for examination in connection with the electronegativity of aluminum. Dr. George Calingaert of the Ethyl Gasoline Corporation has made an investigation of these substances possible by providing several small bulbs containing weighed quantities of the compounds, which were thus handled without exposure to air. Because of the tendency of the methylaluminum dichloride to decompose, it was thought safer to measure it at 25° in benzene solutions, which were made up by breaking the bulbs under weighed quantities of benzene. These solution measurements were carried out by Mr. P. F. Oesper.

APPARATUS AND METHOD

For the gas measurements, the bulbs were broken by a magnetic breaker after having been sealed in the apparatus, which was evacuated before the bulb was broken. In order to save material, a capillary U-tube was used instead of the usual larger U-tube filled with the liquid in question to separate the vapor in the measuring cell from the nitrogen filling the rest of the apparatus and measure any pressure difference between them. The apparatus used for the measurement of the dielectric constants of the vapors was a heterodyne-beat apparatus which had evolved

gradually from the one employed for a large number of measurements some years ago.[1] The electrical circuits had been altered extensively and the large shielding box enclosing them had been thermostated so that the circuits and the precision and reference condensers could be kept at a temperature constant[2] within 0.2°. The stability of the circuits was increased by replacement of old fixed mica condensers by instruments of better quality.

In all the earlier measurements, the sensitivity of the capacity measurements was magnified by connecting the precision condenser on which the readings were made in series with a small fixed mica condenser. Large constant errors discovered in calibration measurements when the apparatus was used after long periods of idleness were attributed to the use of this series arrangement. It was, therefore, replaced by a single condenser of large scale and capacity so small that it could be used for compensating accurately the very small change in the capacity of the measuring condenser produced by changing the pressure of the gas in it. A condenser was constructed for this purpose by removing the plates from an old General Radio Company Type 722 1500 $\mu\mu$f precision condenser, replacing the set of semicircular, movable plates by a single aluminum plate of much reduced size, and restoring two of the fixed plates so that the movable plate could turn between them, the plate separation being greater

[1] K. B. McAlpine and C. P. Smyth, J. Am. Chem. Soc. **55**, 453 (1933).

[2] J. M. A. deBruyne and C. P. Smyth, J. Am. Chem. Soc. **57**, 1203 (1935).

352

than before. The total variable capacity of the condenser was now only about 7 $\mu\mu f$ and its variation was covered by a scale of 2500 divisions which could be estimated to 0.1 division. The actual sensitivity of the setting was 0.2 scale division.

The condenser was calibrated by a modification of the usual method.[3] The arbitrary fixed capacity unit in terms of which it was to be calibrated had to be very small. This small capacity unit was obtained by mounting in parallel with the condenser to be calibrated, already in its final position in the apparatus, a General Radio Company type 722 D precision condenser, to the screw of which a long glass tube was attached and extended through the top of the shielding box. This tube was bent through a right angle just above the top of the box to form a lever. The turning of the lever was restricted to a small angle by two nails driven into the top of the box. When it was turned against one nail, the capacity of the precision condenser was increased. When it was turned from this nail back to the other, the capacity was decreased by a fixed amount, about 0.06 $\mu\mu f$, which formed the unit of calibration of the low capacity precision condenser. This unit could thus be alternately added or subtracted without any change in contacts or leads.

EXPERIMENTAL RESULTS

It has been customary in using this apparatus to make measurements over a range of pressure down to about 20 mm, and to plot the capacity against the pressure. The curves thus obtained are straight lines at the lower pressures, but show very slight curvature at the higher pressures, where deviations from the ideal gas law cause a very slight increase in the number of molecules per unit volume above the number given by the ideal gas law and a corresponding slight increase in the capacity or dielectric constant. The curves thus obtained for trimethylaluminum and dimethylaluminum chloride at several temperatures were typical of those obtained for normal, unassociated vapors, although the experimental errors were somewhat larger than usual because of the instability of the substances, which pre-

vented the use of high temperatures and an extended pressure range. The dielectric constants ϵ calculated from the linear portions of these capacity-pressure curves were used to calculate the polarizations, $P = 22414T(\epsilon-1)/273.1(\epsilon+2)$, T being the absolute temperature. The values thus obtained are given in the second column of Table I. Because of the rapidity of decomposition of these substances in contact with air, their refractive indices were not measured. Their molar refractions, however, were calculated from the refractions of aluminum chloride and aluminum bromide measured by Bredig and Koch[4] and the atomic refractions given in Landolt-Börnstein. The apparent dipole moment μ calculated from the difference between each polarization value and the refraction, 22.9 for trimethylaluminum and 23.1 for dimethylaluminum chloride is given in the third column of Table I. At the bottom of the table are the polarization values of methylaluminum dichloride calculated on the assumption that it is monomeric from the dielectric constants and densities of solutions in heptane containing mole fraction c_2 of solute. The moment is calculated from the difference between the polarization value 103 obtained by extrapolating the P_2-c_2 curve to $c_2=0$ and an estimated refraction 23.

These apparent moment values are quite consistent with one another, for one would expect the moment associated with the Al—Cl bond to be

TABLE I. *Apparent polarization and dipole moment values (molecular association disregarded).*

$T°K$	P	$\mu(\times10^{18})$
Trimethylaluminum		
360.1	57.6	1.43
384.1	56.7	1.46
398.0	50.4	1.34
Dimethylaluminum chloride		
324.8	73.1	1.63
348.1	68.5	1.61
371.1	67.6	1.65
395.3	66.7	1.69
416.4	66.7	1.73
Methylaluminum dichloride ($T=298.1°K$)		
c_2		
0.000000	103	1.96
.006209	90.5	
.006683	87.9	
.014799	73.7	

[3] C. P. Smyth, *Dielectric Constant and Molecular Structure* (The Chemical Catalog Company, New York, 1931), p. 52.

[4] M. A. Bredig and F. K. V. Koch, Zeits. f. physik. Chemie **B24**, 187 (1934).

R. H. WISWALL, JR. AND C. P. SMYTH

considerably larger than that of the Al−C bond, so that each replacement of a methyl group by a chlorine atom should increase the moment, as it does. However, the results of vapor density measurements presented by Dr. A. W. Laubengayer of Cornell University at the Detroit meeting of the American Chemical Society and very kindly communicated by him to the authors indicate that trimethylaluminum exists largely as a dimer $[(CH_3)_3Al]_2$ in the region of temperature and pressure employed in the present measurements. The aluminum halides also are known[5] to exist as dimeric molecules in the vapor state below 400°C. It is, therefore, desirable to examine the polarization values calculated at each pressure and temperature for evidence of molecular association and of its effect upon the moment values. These polarization values at pressure p are listed in Table II in the order in which they were measured at each temperature with the object of showing whether appreciable decomposition of the material occurred during the course of the measurements.

DISCUSSION OF RESULTS

The polarization values in Table II show no regular dependence upon pressure such as might be expected to arise from a pressure-dependent equilibrium between a monomer and a dimer, nor is there any appreciable drift with time to give evidence of chemical change. In order to analyze the effect of molecular association upon the apparent values of the polarization, the values of the equilibrium constant K for the dissociation of the dimer, $(CH_3)_6Al_2$, were calculated for the temperatures here used by plotting $\log K$ for the values of K given us by Dr. Laubengayer against $1/T$ and interpolating. The degree of dissociation α was then calculated at each pressure p as $\alpha = [K/(4p+K)]^{\frac{1}{2}}$. The observed polarization P may be regarded as a combination of the polarization P_1 of the dimer and P_2 of the monomer and written $P = c_1P_1 + c_2P_2$, where c_1 and c_2 are the respective mole fractions. As $c_1 = (1-\alpha)/(1+\alpha)$ and $c_2 = 2\alpha/(1+\alpha)$, substitution and rearrangement gives $P_2 = 1/2[(P-P_1)/\alpha + (P+P_1)]$. The values of P_2 were calculated at each pressure and

[5] See K. J. Palmer and N. Elliott, J. Am. Chem. Soc. **60**, 1852 (1938).

TABLE II. *Dependence of polarization upon pressure and temperature.*

p(MM)	P	p(MM)	P
Trimethylaluminum			
$T=360.1°K$		$T=398.0°K$	
27.8	58.0	20.0	50.0
46.8	57.5	55.0	52.5
66.7	57.5	76.8	50.1
58.4	57.9	100.6	49.6
36.2	60.0	123.1	50.4
$T=384.0°K$		160.6	54.5
22.3	65.6		
46.9	60.9		
103.0	56.0		
75.9	54.6		
124.9	56.4		
154	57.7		
Dimethylaluminum chloride			
$T=324.8°K$		$T=395.3°K$	
13.6	71.7	31.3	66.8
38.4	72.3	65.5	66.3
49.8	74.9	91.0	67.1
28.0	74.0	132.5	66.2
$T=348.1°K$		166.4	66.8
16.9	74.6	189.3	67.2
39.5	68.2	$T=416.4°K$	
83.4	68.9	36.1	65.5
99.9	69.1	63.2	66.8
126.1	72.5	107.5	66.6
$T=371.1°K$		141.7	66.0
10.0	(74.3)	179.9	66.9
53.2	65.7	209.5	67.0
91.7	65.9		
132.1	65.9		
173.6	66.5		
195.3	67.2		

temperature by assigning to the dimer the polarization value $P_1 = 46$, arrived at by assuming the dimer to be a symmetrical structure with zero moment and polarization consequently equal approximately to its molar refraction, which should be approximately double that for the monomer, 23. The values of P_2 calculated by the above expression have probable errors of, at least, 10 percent, because of the division of the small difference $P-P_1$ by the small values of α, and show a tendency to be larger the smaller the value of α, instead of being practically independent of pressure as they should be. This behavior naturally follows from the fact that the observed values of P are almost independent of pressure. Moreover, as the degree of dissociation increases with rising temperature, the values of P_2 fall off more rapidly than they should according to the Debye equation. Consequently, the moment values calculated from them decrease with rising temperature, the values being about 2.4×10^{-18} at 360.1°K, 2.2 at 384.1°, and

1.6 at 398.0°. As there is a distinct possibility that the molar refraction of the dimer may be a little higher than 46, and the atomic polarization should raise it a little more, the calculations were repeated with a value of 50 for P_1. The average moment value at each temperature was thereby reduced by about 0.3×10^{-18}. By using a value $P_1 = 61$, the moment value was reduced approximately to zero at 398°, but was still considerable at the two lower temperatures. However, 50 is close to the upper limit of the value which can reasonably be assigned to P_1, the polarization of the dimer, unless its molecule has an altogether abnormal atomic polarization or a small permanent moment because of an unsymmetrical structure. As there is more of the monomer present at the highest temperature, more weight should, probably, be given to the moment value found there. The logical conclusion to be drawn from these results is that the monomer $(CH_3)_3Al$ has a moment value $1.6 \pm 0.8 \times 10^{-18}$, which is close to the value obtained when all association is neglected. It must, however, be borne in mind that the curious behavior which has been described, possibly the result of an unsuspected amount of decomposition, and the remote possibility of an abnormally high atomic polarization leave an element of doubt as to the validity of the conclusion.

Because data are not available as to the association of dimethylaluminum chloride and methylaluminum dichloride, which, in view of the association of trimethylaluminum and the aluminum halides, should be strongly associated, moment values cannot be obtained for their monomeric forms. It can, however, be concluded that the molecules possess considerable moments as indicated by the apparent values in Table I.

In view of the fact that trimethylboron and boron trichloride have symmetrical planar structures,[6] one would anticipate a similar structure for trimethylaluminum, which, of course, would have zero dipole moment. However, there is a pronounced difference between the two boron compounds and the corresponding aluminum compounds in that the former exist as monomers while the latter exist largely as dimers. The

[6] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, second edition, 1940), p. 88, 233.

results of electron diffraction have been interpreted[5] as showing the two aluminum atoms of the dimeric aluminum halides to be held together by two halogen atoms shared in common between them, each aluminum being at the center of a distorted tetrahedron with a halogen atom at each of the four corners of the tetrahedron, one edge of which is shared with the other tetrahedron. If this structure is correct for the aluminum halides, one would expect double molecules of dimethylaluminum chloride and methylaluminum dichloride to form through the holding of two halogen atoms in common between two aluminum atoms. The dimeric form of the dimethylaluminum chloride,
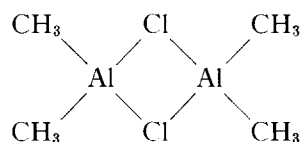
would then have zero moment, while the monomeric form would have a moment dependent upon the difference between the $Al-Cl$ and the $Al-C$ bond moments, which should be considerable. The dimer of methylaluminum dichloride should exist in a *cis*-form having a considerable moment and a *trans*-form having zero moment, while the monomeric molecule with two $Al-Cl$ bond moments should have a moment considerably larger than that of the monomeric molecule of dimethylaluminum chloride.

The trimethylaluminum molecule contains nothing to form a link between two aluminum atoms but the orbitals of the aluminum atoms. One must, therefore, ascribe to the dimer a more or less ethane-like structure with the two aluminum atoms directly bonded to each other. In view of this bonding here, one may wonder if there may not be a strong possibility of direct aluminum-aluminum bonding in the dimeric molecules of the halogenated aluminum compounds. Since there is evidently a marked difference between the behavior of the boron and the aluminum compounds, it is not unreasonable to suppose that a difference may exist between the structures of the $(CH_3)_3B$ and the $(CH_3)_3Al$ molecules. The sp^2 configuration which one would naturally ascribe to the boron and aluminum orbitals in these molecules has been shown by

Pauling[7] to give rise to a trigonal plane structure, a pyramidal structure also being possible but less stable because of repulsive forces.[8] The larger size of the aluminum atom would make these repulsive forces less in the $(CH_3)_3Al$ than in the $(CH_3)_3B$ molecule, thereby increasing the stability of a possible pyramidal structure. If the pyramidal structure gave the tetrahedral angle 110° to the $C-Al-C$ valence angle, the $Al-CH_3$ moment would be the same as that roughly calculated for the molecule, 1.6×10^{-18}, and the $Al-C$ bond moment, which presumably acts in the opposite direction to the $H-C$ moment, would be 1.6 increased by the estimated value 0.3 of the $H-C$ moment, or 1.9×10^{-18}. Reduction in the size of the $C-Al-C$ valence angle reduces the value calculated for the $Al-C$ moment. If the $C-Al-C$ angle is 90°, the value calculated for the $Al-C$ bond moment is 1.2×10^{-18}, while

if the angle is greater than 110°, the $Al-C$ bond moment is greater than 1.9×10^{-18}. These very rough values estimated for the $Al-C$ bond moment are considerably smaller than one would expect for the aluminum-halogen bond moments and are consistent with the small magnitude of moment and predominantly covalent character attributed to metal-carbon bonds.[9]

Because of the considerable importance of the structures of aluminum compounds, it has seemed desirable to present these experimental data in spite of the difficulties which molecular association introduces into their interpretation. Although these difficulties are such as to render any conclusions somewhat uncertain, the data do indicate a strong probability that the monomeric trimethylaluminum molecule has a pyramidal structure and that the aluminum-carbon bond is largely covalent.

[7] Pauling, J. Am. Chem. Soc. 53, 1367 (1931).
[8] G. E. Kimball, J. Chem. Phys. 8, 188 (1940).

[9] G. L. Lewis, P. F. Oesper and C. P. Smyth, J. Am. Chem. Soc. 62, 3243 (1940).

Induction and Dipole Moment in Chloro- and Nitroparaffins

R. H. WISWALL, JR. AND C. P. SMYTH
Frick Chemical Laboratory, Princeton University, Princeton, New Jersey
(Received January 9, 1941)

The dielectric constants of the vapors of the butyl chlorides, methyl chloroform, nitromethane, α- and β-nitropropane, and 2-methyl-2-nitropropane have been measured over a range of temperature and pressure and used to calculate the dipole moments of the molecules of these substances. The dipole moment increases from normal to secondary to tertiary butyl chloride much less than indicated by the apparent moments previously measured in solution, it being shown that the apparent solution values for the primary and secondary compounds are lowered by solvent effect. The moments found for α- and β-nitropropane and 2-methyl-2-nitropropane are indistinguishable from one another, but are slightly larger than that of nitromethane. Examination of the molecular models shows that the moment differences found are approximately those to be expected from the inductive effects, with the exception of the large difference between chloroform and methyl chloroform where it can only be said that induction is a major cause of the difference.

INDUCTION is often such an important factor in the interpretation of dipole moment data that it has seemed desirable to check up on certain ideas as to induction effects which were originally based upon moment values determined in solution and thus subject to the uncertainties introduced by solvent effects. This checking up process has been carried out by measuring the dipole moments in the vapor state of the four butyl chlorides and methyl chloroform previously measured in solution and of four nitroparaffins, two of which had previously been measured as vapors. The measurements were carried out with the modified heterodyne beat apparatus previously described,[1-3] the

[1] K. B. McAlpine and C. P. Smyth, J. Am. Chem. Soc. 55, 453 (1933).
[2] J. M. A. de Bruyne and C. P. Smyth, J. Am. Chem. Soc. 57, 1203 (1935).
[3] R. H. Wiswall and C. P. Smyth, J. Chem. Phys. 9, 352 (1941).