THE ELECTRIC MOMENTS OF SOME SUBSTANCES IN THE VAPOR PHASE

Thesis for the Degree of M. S.
MICHIGAN STATE UNIVERSITY
Lenore Ho
1957

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A Thesis

Submitted to

the School of Graduate Studies

of Michigan State University

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In Partial Fulfillment

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Master of Science

Department of Chemistry

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by

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November 1957

THE KINETICS [illegible] OF [illegible] IN [illegible] PHASE

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AN ABSTRACT

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Approved M. T. Rogers

THE ELECTRIC MOMENTS OF SOME COMPOUNDS IN THE VAPOR STATE

AN ABSTRACT

The electric moments of four compounds of oxygen, nitrogen and phosphorus have been measured in the vapor phase. The substances studied, and the electric moments found in this investigation, are: isopropyl ether 1.13D, tert-butylamine 1.25D, trifluoroacetic anhydride 1.49D, and phosphorus trichloride 0.98D. Only isopropyl ether had been studied in the vapor state previously and the value reported by Le Fevre, 1.13D, is in excellent agreement with the value reported here.

The electric moment of phosphorus trichloride found in this work in the vapor state may be compared with the values of 0.80D (54) and 0.90D (55) reported in the literature for phosphorus trichloride dissolved in carbon tetrachloride and benzene, respectively. Since the electric moments of most substances are 0.1-0.2D lower in solution than in the gas phase the behavior of phosphorus trichloride is normal. tert-Butylamine, however, has a lower moment in the vapor phase than the value 1.30D (44) found in benzene solution. This anomalous behavior has been reported in the literature for other amines; thus, triethylamine has a moment of 0.87D in the vapor state but 0.90D in benzene solution.

The electric moment of trifluoroacetic anhydride in the vapor state was found in this work, to be much lower than that reported in the literature for acetic anhydride ($\sim$ 2.80). The moment calculated for trifluoroacetic acid from bond moments is 1.42D assuming that the angle C–O–C is 110° and the angle O–C=O is 125° in the anhydride. Since the agreement between observed and calculated moments is so good the bond angles in trifluoroacetic anhydride are probably not far from the values assumed above.

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CHAPTER I

INTRODUCTION

The electric moment of a molecule is of importance in determining details of its electronic structure and atomic arrangement. The observed electric moment may be compared with a value calculated from known bond moments and bond angles. Differences between the observed and calculated electric moments are then indicative of resonance or inductive effects or, in some cases, altered bond angles.

In the present investigation the electric moments of a group of compounds of phosphorus, nitrogen and oxygen have been determined to obtain information concerning their electronic structures. These molecules all are characterized by the presence of unshared pairs of electrons on the central atom; such molecules frequently show anomalous electric moments.

Although dipole moments are usually measured in solution such values are always subject to some uncertainty as a result of solvent effects. To avoid such uncertainties the electric moments of the compounds studied here were measured in the vapor phase.

CHAPTER II

APPARATUS AND METHODS

I. [illegible]

In general measurements of dielectric constant are based on measuring the capacitance C_o of an empty condenser and the capacitance C of the condenser when filled with the dielectric material in question.

There are three principal methods of measuring the dielectric constant: the capacitance-bridge method (1-11), the resonance method (10-12), and the heterodyne method (12-23), which was employed in this investigation.

Other methods are also used for measurement of dielectric constant. The microwave method (24-27) which depends on measuring the wave-length of electromagnetic waves in air and then in the dielectric material, has become very important.

II. [illegible]

General Design (28). The block diagram of the heterodyne-beat apparatus is represented in Figure I. Two oscillators, one fixed and the other variable, have been used to give two different radio-frequency signals f_o and f respectively. These two frequencies are mixed in the frequency mixer tube, then produce a beat note of frequency $f - f_o$ which is then

compared with a standard 400 cycle frequency on the oscilloscope by observing the Lissajous figure. f can be defined as

$$f = \frac{1}{2\pi\sqrt{LC}} \qquad (29)$$

where L is inductance, C is capacitance.

If f is greater than f_o, then an increase of total capacitance will counterbalance the frequency of the beat note, until f is equal to f_o (beat frequency is equal to zero). A constant frequency source of 400 cycles was used as reference instead of the zero beat, because the oscillators tend to lock in near zero beat. The constant-frequency source was compared with the beat frequency on a cathode-ray oscilloscope, by observing the Lissajous figure, until a circle was obtained.

Sensitivity and Accuracy. The oscillator instability determines the over-all sensitivity or the smallest measurable capacitance change. The fixed series condenser was chosen so that a change of 0.1 cycle per second can be detected on the oscilloscope. The capacitance can be measured to the order of 0.001 micromicrofarad. This method has been used by Chien (18).

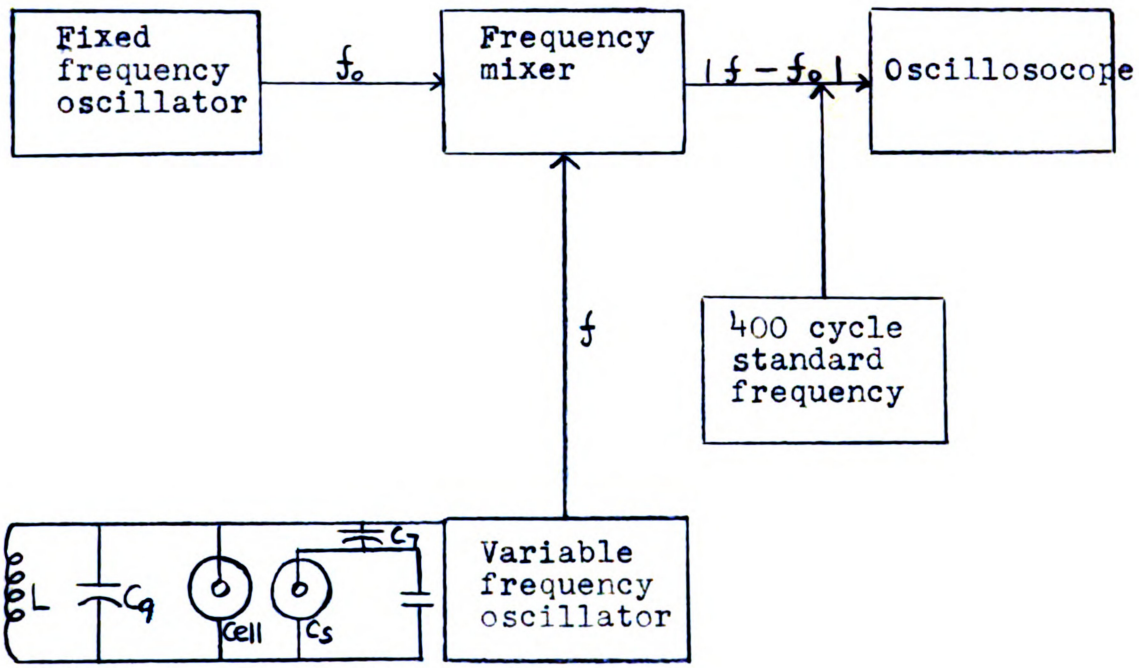

Figure I. Block Diagram Illustrating The Principle of The Heterodyne-beat Apparatus

Precision Condenser. A General Radio precision condenser, type 722, with a capacitance range of 1100 micromicrofards was used as the standard condenser. Another condenser C_7 was placed in series with the precision condenser to decrease the effective capacitance (see Figure I).

The total capacitance can be written as,

$$C = \frac{C_s \cdot C_7}{C_s + C_7}$$

where C_s is the standard condenser. Another condenser C_9 (a General Radio type 380-N mica decade condenser) was placed in parallel with the standard condenser to make the net capacitance more nearly linear with the reading on the standard condenser. Therefore the total capacitance would be,

$$C = \frac{C_7^2}{(C_s + C_9 + C_7)}$$

Then differentiating with respect to C_s gives,

$$\frac{dC}{dC_s} = \frac{C_7^2}{(C_s + C_9 + C_7)^2}$$

Since C_9 is much larger than C_s the change of total capacitance will be more linear than before.

Calibration of Precision Condenser. The calibration was made possible by using a primary standard capacitance (See Figure II) which consisted of a cylinder and a center rod, the opposite ends of the rod had different diameters. When

the inner rod was moved along its axis, a small increment in capacitance was obtained. The center rod and the drum was ruled with 1400 units per inch. There were 1.4800 micromicrofarads capacitance change per inch, that means 0.001057 micromicrofarads per drum unit. The center portion of the scale was used for the calibration, since it was the most linear part of the scale. This primary capacitance was built by J. L. Speirs (30) and designed by Conner (31). The precision condenser was calibrated with C_2 set at 2 microfarads, which setting was used for all the dielectric constant measurements throughout the entire investigation. From a plot of standard condenser readings versus capacitance reading on primary condenser, the capacitance change on introducing the gas into the cell was obtained.

Dielectric Constant Cell. The dielectric constant cell (see Figure III) can only handle gases with low boiling points which are not corrosive to glass or nickel. It consisted of a series of nickel-plated copper cylinders which were insulated by small Teflon spacers. One set of cylinders were grounded, the other was at high potential. There were tungsten leads sealed through the glass which were then connected to the heterodyne-beat apparatus (32). The replaceable capacitance of the cell is about 350 micromicrofarads. It was necessary to calibrate the cell for

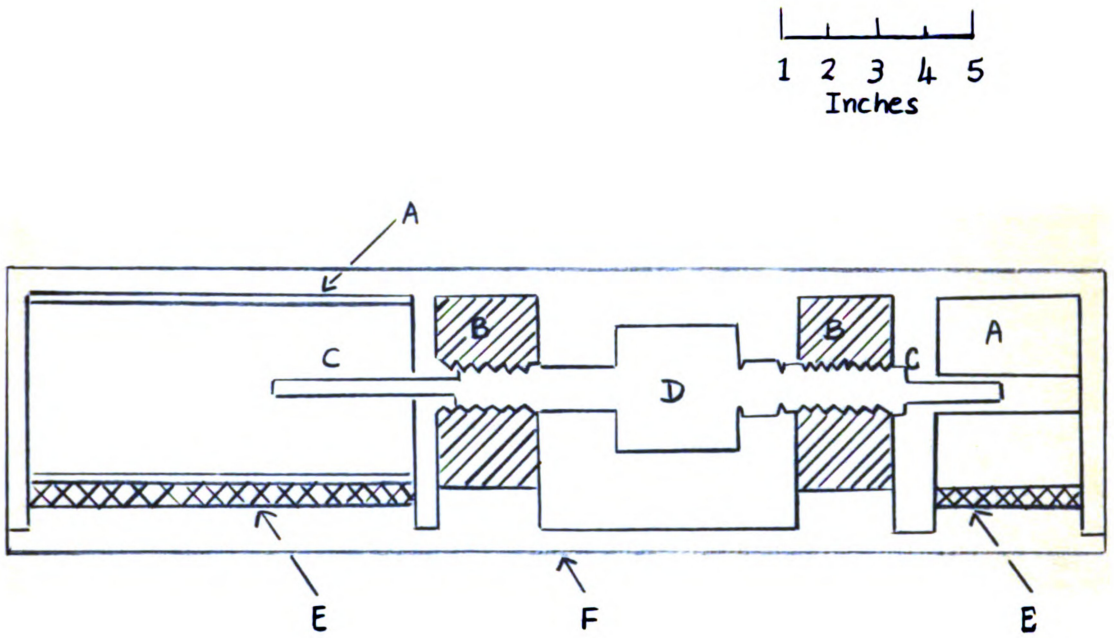

Figure II. Primary Standard Capacitor Used for Calibrating General Radio Precision Condenser.

A Coaxial cylinders
B Threaded blocks
C Center rod
D Graduated drum
E Mycalex insulators
F Grounded base and case

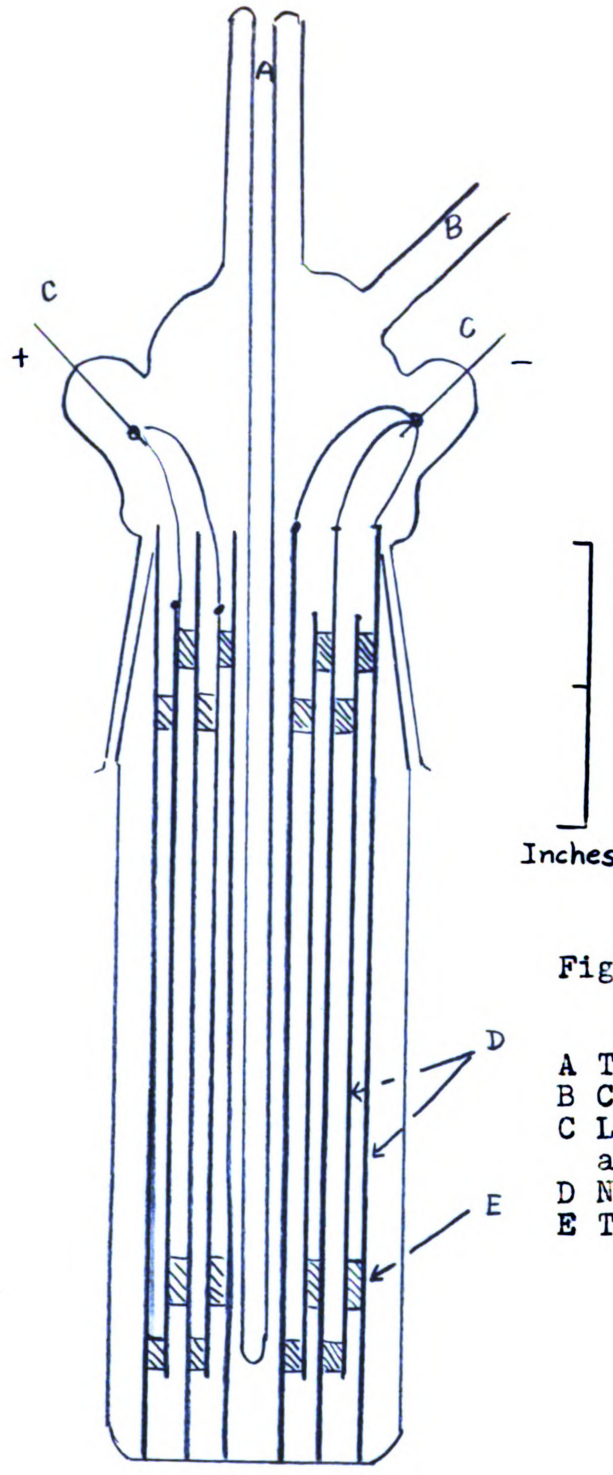

Figure III. Dielectric Constant Cell for Non-corrosive Gases.

A Themocouple well
B Connection to vacuum line
C Leads to heterodyne-beat apparatus
D Nickel-plated copper cylinder
E Teflon insulators

each temperature, since it was found to change slightly with temperature. Ammonia[1] was used to calibrate the cell at each temperature.

Gas-Handling System. The glass vacuum system is shown in Figure II. The trap leading to the pump is cooled with Dry Ice-Isopropanol mixture to prevent gases entering the pump. Another trap, which could be removed, was used to introduce gases. A mercury manometer was used to measure the pressure of the gases under investigation and also that of the gas used for calibration. The system could be evacuated.

Temperature-Controlled Bath. The heating system, thermocouple and the cell were all immersed in a copper can which was filled with Arochlor 1248[2] (chlorinated biphenyl). The bath was used from room temperature to around 75°C. Since the vapors of Arochlor 1248 are toxic an air blower was used to pull the vapors into the hood.

Thermoregulator and Temperature Measurement (26). A thermistor[3] (temperature-sensitive element) was used in a Wheatstone bridge circuit. In order to control the current, the heater was in series with a saturable reactor. The

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[1]From the Matheson Co., Inc., E. Rutherford, N.J., Joliet, Ill.

[2]From Monsanto Chemical Company, St. Louis, Mo.

[3]A type 14P thermistor, manufactured by the Western Electric Company, New York, N.Y. was used.

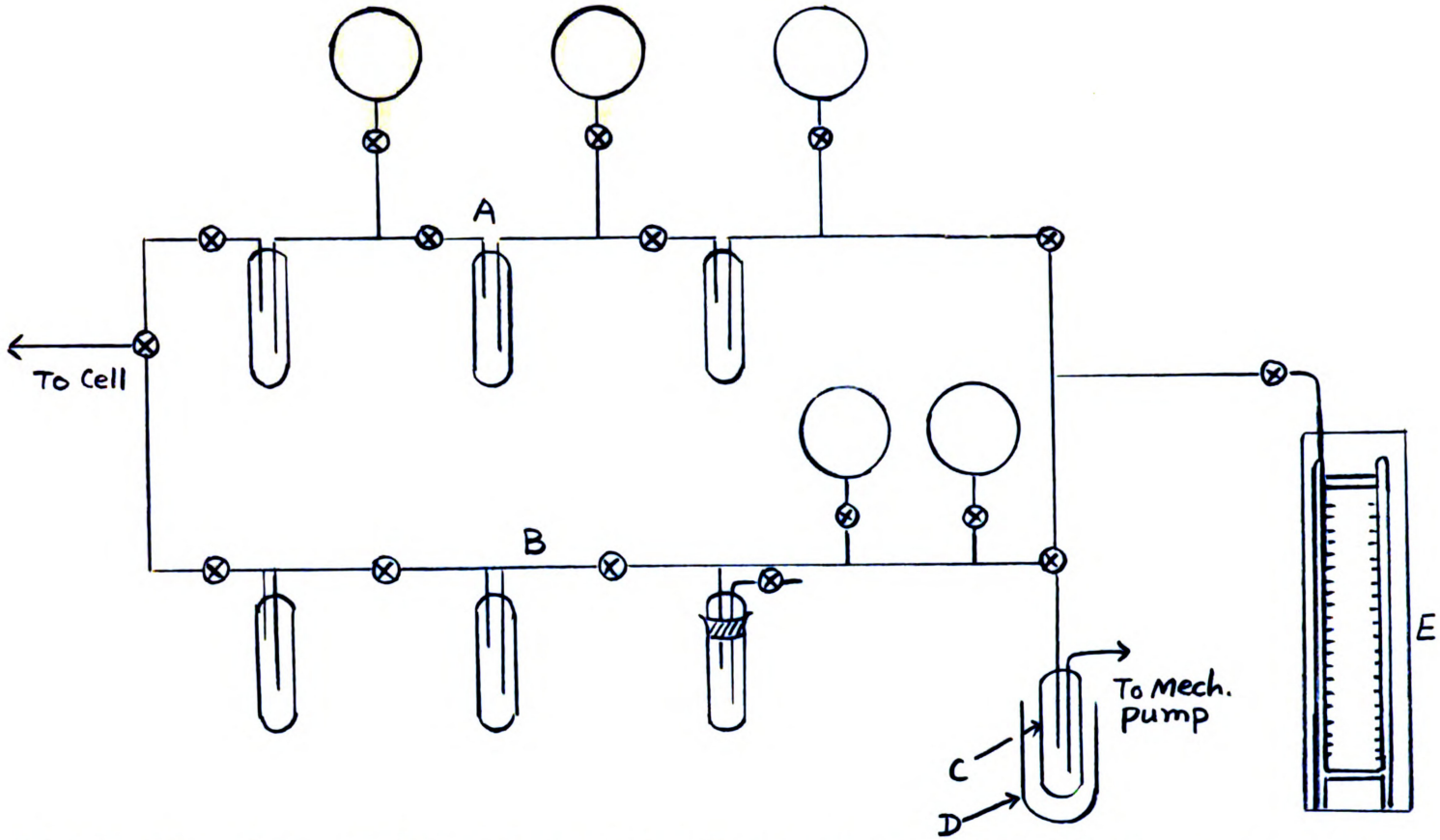

Figure IV. Gas Handling System for Non-corrosive Gases (Vacuum line)

A,B Series of traps used for distilling and storing gases being measured
C Glass cold traps for pump protection
D Dry ice-isopropanol mixture bath
E manometer for pressure measurement
⊗ Glass vacuum stopcocks

temperature could be controlled to ± 0.05°C. The thermoregulator was designed by Purwell, Peterson and Rathmann (33).

Temperature measurements were made using copper-constantan (No. 22 wire) thermocouples[1] and a precision potentiometer.[2] One thermocouple was immersed in the bath, and another was placed in an ice-water mixture as a reference. Since the temperature within the cell was slow to reach equilibrium, it was necessary to wait over-night for temperature equilibrium. The readings from the potentiometer were converted to degrees Centigrade by making a large plot of millivolts *versus* degrees (34).

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[1]The thermocouple wires were purchased from the Wheelco Instruments Company, Chicago, Illinois.

[2]A type K potentiometer of Leeds and Northrup Company, Philadelphia was used.

CHAPTER III

THEORETICAL BACKGROUND

Debye Equation (11)(14) Assuming the molecule to be a rigid system of charges, the potential energy u of the molecule is given by the following equation,

$$u = -(mF) \qquad (I)$$

where m is its electric moment along the field direction and F is the intensity of the field.

Since the axis will ordinarily make an angle θ with the direction of F,

$$u = -\mu F \cos\theta \qquad (II)$$

where μ is the absolute value of the electric moment. The number of molecules distributed with the axes of their dipoles pointing in the direction within a solid angle $d\Omega$ is,

$$A e^{-(u/kT)} d\Omega$$

where A is a constant depending on the molecules considered, k is the molecular gas constant equal to 1.38×10^{-16}, and T the absolute temperature. The average moment per molecule in the direction of the field is,

$$\bar{m} = \frac{\int A e^{(\mu F/kT)\cos\theta} \mu \cos\theta \, d\Omega}{\int A e^{(\mu F/kT)\cos\theta} d\Omega} \qquad (III)$$

Since $u = -\mu F \cos\theta$ (II)

Substituting $$x = \frac{\mu F}{kT} \qquad (IV)$$

and $$y = \cos\theta \qquad (V)$$

since $$d\Omega = 2\pi \sin\theta \, d\theta \qquad (VI)$$

is found that,

$$\frac{\bar{m}}{\mu} = \frac{\int_{-1}^{+1} e^{xy} y \, dy}{\int_{-1}^{+1} e^{xy} \, dy} \qquad (VII)$$

Integrating numerator and denominator and simplifying, we get,

$$\frac{\bar{m}}{\mu} = \frac{e^{x} + e^{-x}}{e^{x} - e^{-x}} - \frac{1}{x} \qquad (VIII)$$

Since $$\frac{e^{x} + e^{x}}{e^{x} - e^{x}} = \coth x \qquad (IX)$$

$$\frac{\bar{m}}{\mu} = \coth x - \frac{1}{x} = L(x) \qquad (X)$$

For small value of x, $L(x)$ can be expanded in the series (35-36).

$$L(x) = \frac{x}{3} - \frac{x^3}{45} + \cdots\cdots \qquad (XI)$$

Since x is very small we can replace $L(x)$ by the first term of the series,

$$L(x) = \frac{x}{3} \qquad (XII)$$

with the result that,

$$\bar{m} = \frac{\mu^2}{3kT} F \qquad (XIII)$$

This mean moment plus the induced moment, which has been temporarily disregarded, may be added to give the total mean moment in the direction of the field which is,

$$\bar{m} = \alpha_0 F + \frac{\mu^2 F}{3kT} = (\alpha_0 + \frac{\mu^2}{3kT}) F \qquad (XIV)$$

If we include α_0 the distortion polarization and $\frac{\mu^2 F}{3kT}$ the orientation polarization then the total polarization is,

$$\alpha = \alpha_0 + \frac{\mu^2}{3kT} \qquad (XV)$$

the more general expression

$$\frac{\epsilon-1}{\epsilon+2}\frac{M}{d} = P = \frac{4\pi N}{3}\alpha = \frac{4\pi N}{3}\left(\alpha_0 + \frac{\mu^2}{3kT}\right) \qquad (XVI)$$

is obtained where P is the total polarization.

The Calculation of Electric Moments (11).

A. First method for the measurement of dipole moment.

The molar polarization P is

$$P = \frac{4\pi N}{3}\left(\alpha_0 + \frac{\mu^2}{3kT}\right) \qquad (XVI)$$

P can also be calculated from measurement of the dielectric constant ϵ and the density ρ, as following:

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

P may be found at different temperatures and plotted as a function of the variable 1/T. There are two types of behavior. First, the molecule is non-polar and its electric moment μ is zero. Second, P is dependent on temperature when the molecule is polar. Let the curve be represented by the formula,

$$P = a + b/T \qquad (XVIII)$$

where a and b are constants, then

$$b = \frac{4\pi}{9}\frac{N}{k}\mu^2 \qquad (XIX)$$

Where $N = 6.06 \times 10^{23}$

and $k = 1.37 \times 10^{-16}$, and

$$\mu = 0.01281 \sqrt{b} \times 10^{-18} \text{ e.s.u.} \qquad (\text{V})$$

B. Second Method for the measurement of dipole moment. (11)

Let us consider the fundamental formula for the molar polarization

$$P = \frac{4\pi}{3} N \left(\alpha_0 + \frac{\mu^2}{3kT} \right) \qquad (\text{VI})$$

The part $(\frac{4\pi}{3})N\alpha_0$ which we call P_0 is independent of temperature. If we can measure P at any one temperature, and obtain P_0 by another method, then

$$\frac{4\pi}{3} \frac{N\mu^2}{3kT} = P - P_0 \qquad (\text{VII})$$

where $N = 6.06 \times 10^{23}$ and $k = 1.37 \times 10^{-16}$

$$\therefore \mu = 0.01281 \times 10^{-18} \sqrt{(P-P_0)T} \text{ e.s.u.} \qquad (\text{VIII})$$

If we are dealing with gases and vapors only,

$$R = \frac{n^2 - 1}{n^2 + 2} \frac{M}{\rho} \qquad (\text{VIII})$$

is a suitable approximation to P_0. From the square of the refractive index n we can find a value for R, which is the molar refraction. Therefore we can calculate the electric moment μ as follows:

$$\mu = 0.01281 \times 10^{-18} \sqrt{(P_M - R)T} \text{ e.s.u.} \qquad (\text{IX})$$

where P_M is called the total molar polarization and can be obtained from the following expressions:

$$P_M = \left(\frac{\epsilon - 1}{\epsilon + 2}\right) V_M \qquad (XV)$$

and

$$V_M = \frac{RT}{p} \qquad (XVI)$$

CHAPTER IV

REVIEW OF LITERATURE

Isopropyl Ether. The dipole moments of eight ethers were measured in benzene solution (37). The molar refraction MR_D was calculated in each case from the atomic refractions. (38) The dipole moments μ calculated by the method of Hedestrand (39) are given in Table I.in Debye units. The moment of 1.29D for diethyl ether in benzene is in good agreement with the value of 1.27D given by Hassel and Uhl (40). The values of 1.26 and 1.22D obtained for di-n-butyl ether and ethyl n-butyl in benzene respectively, are to be compared with the values 1.22 and 1.24D obtained by Li and Terry (41). Groves and Sugden (42) give the value 1.18D for the moments of the normal symmetrical ethyl, propyl and butyl ethers in the vapor state. It is interesting to note that the average of the moment of the symmetrical ethers (1.28) is larger than that of the unsymmetrical ethers (1.21D). Symmetry in ethers might be expected to stabilize hyperconjugation structures. The dipole moments of some symmetrical and unsymmetrical ethers are shown in Tables I and II.

TABLE I

Dipole Moments of Symmetrical Ethers (43)

Ethers	Me_2O	Et_2O	Pr^n_2O	Pr^i_2O	Bu^n_2O
μC_6H_6	1.25D	1.26D	1.13D	1.26D	1.09D
(μ gas) calc.	1.26D	1.21D;1.15D	1.17D;1.21D	1.23D	1.13D;1.28D
(μ gas) found	1.29D	1.17D	1.18D	1.13D	1.17D

TABLE II

Dipole Moments of Unsymmetrical Ethers (37)
(in Benzene Solution)

Substances	μ Debye
Methyl-n-propyl ether	1.24
Ethyl n-propyl ether	1.16
Methyl n-butyl ether	1.29
Ethyl n-butyl ether	1.12
n-Propyl n-butyl ether	1.17

tert-Butylamine. Two butylamines were studied in dioxane solution (44) to ascertain whether the molecular interaction involves the formation of hydrogen bonds between the amino-hydrogen atoms and one of the oxygen atoms of the dioxane molecule. n-Butylamine and tert-butylamine have sufficiently low volatility to permit easy and accurate manipulation, and represent compounds with the amino-group linked to a primary and tertiary carbon atom respectively. The following are the dipole moment measurements in benzene and dioxan:

TABLE III

Comparison of Polarization Data For Amines In Benzene And Dioxan Solution (44)

	$P_{2\infty}$ Benzene	$P_{2\infty}$ Dioxan	μ(D) Benzene	μ(D) Dioxane
n-Butylamine	61.13	60.14	1.322	1.305
tert-Butylamine	61.23	61.28	1.322	1.322

It cannot be inferred conclusively from these results that no hydrogen bonding occurs between the butylamines and dioxane, but this appears improbable, as even in the absence of mesomeric effects the apparent dipole moment should change (45).

Trifluoroacetic Anhydride. The dielectric constant of trifluoroacetic anhydride was measured (46-47). The

value obtained (ϵ = 2.7 at 25°C) is considerably lower than that for trifluoroacetic acid (ϵ = 8.2 at 25°C). The dielectric constant of acetic anhydride (ϵ = 2.1 at 25°C) is similarly smaller than the dielectric constant of acetic acid (ϵ = 6.3 at 25°C).

Very approximate calculations have also indicated that the inductive effect of one C-F dipole should lower the moment of a second C-F dipole attached to the same carbon atom by about 0.22 (48) while one C-Cl dipole should lower the amount of another C-Cl dipole by about 0.36×10^{-18}.

Phosphorus Trichloride. The molar polarizations of PCl_3 and PBr_3 were measured in C_6H_6 and CCl_4 solution (49). The observed values in cc. are: PCl_3 in C_6H_6 48.2 (10°), 46.8 (25°) 45.6 (40°); PCl_3 in CCl_4, 43.8 (-25°), 42.2 (0°), (25°); PBr_3 in C_6H_6, 43.2 (10°), 41.5 (25°), 40.5 (40°); PBr_3 in CCl_4, 47.4 (-25°), 46.5 (0°), 45.8 (25°). From these data the dipole moments were found to be 1.00D and 0.52D respectively.

CHAPTER V

EXPERIMENTAL DATA AND RESULTS

TABLE IV

Data For The Calibration of The
General Radio Precision Condenser

Units on Precision Condenser	Units on Primary Standard Capacitor	A*	Capacitence $\mu\mu f \times 10^2$
100	1254.1	0.0	0
120	1302.8	48.7	5.148
140	1348.0	93.9	9.932
160	1390.9	136.8	14.460
180	1435.7	181.6	19.195
200	1477.8	223.7	23.645
220	1520.6	266.5	28.169
240	1559.0	304.9	32.228
260	1596.1	342.0	36.149
280	1634.7	380.6	40.229
300	1671.3	417.2	44.098
320	1707.2	453.1	47.893
340	1743.4	489.3	51.719
360	1776.3	522.2	55.197
380	1810.0	555.9	58.759
400	1847.7	593.6	62.744
420	1878.6	625.5	66.115
440	1912.0	657.9	69.534
460	1960.3	706.2	74.645
460	1197.2	706.2	74.645
480	1214.9	723.9	76.516
500	1244.2	753.2	79.613
520	1271.0	780.0	82.446
540	1302.3	811.3	85.754
560	1330.1	839.1	88.693
580	1356.3	865.3	91.462
600	1382.0	891.0	94.179
620	1410.0	919.0	97.138
640	1436.5	945.5	99.939
660	1461.0	970.0	102.529
680	1486.5	995.5	105.224
700	1512.2	1021.2	107.941

TABLE IV (continued)

Units on Precision Condenser	Units on Primary Standard Capacitor	A*	Capacitance $\mu\mu f \times 10^2$
720	1536.2	1045.2	110.478
740	1559.0	1064.0	112.[illegible]
760	1582.3	1091.3	115.370
780	1604.9	1113.9	117.759
800	1627.5	1136.5	120.[illegible]
820	1650.4	1159.4	122.[illegible]
840	1671.1	1180.1	124.737
860	1693.0	1202.0	127.051
880	1715.0	1224.0	129.[illegible]
900	1735.9	1244.9	131.[illegible]
920	1756.9	1264.9	133.[illegible]
940	1775.0	1284.0	135.[illegible]
960	1796.0	1305.0	137.[illegible]
980	1815.2	1324.2	139.[illegible]
1000	1834.5	1344.5	142.114
1020	1853.7	1362.7	144.[illegible]
1040	1872.3	1379.3	145.[illegible]
1060	1888.0	1397.0	147.663
1080	1905.1	1414.1	149.470
1100	1923.5	1432.5	151.415

*Column A gives the total number of units on the primary standard capacitor that correspond to the number of units covered on the precision condenser.

TABLE V

Dielectric Constants of Ammonia Vapor
At Several Temperatures (50)

Temperature C°	$(\epsilon-1) \times 10^6$
20.95	5826
30.72	5522
47.59	5040
58.63	4916
71.44	4581
80.33	4369
92.21	4062
116.12	3493

TABLE VI

Calibration Data For Dielectric Cell

Pressure mm of Hg	Condenser Reading	Capacitance $\mu\mu f \times 10^2$	Pressure mm of Hg	Condenser Reading	Capacitance $\mu\mu f \times 10^2$
Calibration at 23.75°C			Calibration at 36.75°C		
395	290.3	42.6	205	143.5	11.2
339	369.6	57.0	174	175.8	15.6
295	436.0	68.5	146	205.8	20.2
246	510.3	82.3	116	239.6	25.2
195	611.4	96.0	91	267.6	29.2
141	720.9	113.6	67	302.1	34.0
93	828.4	123.6	32	347.3	40.8
40	961.9	138.0	0	394.0	48.2
0	1043.7	149.8			
			204	131.0	7.2
250	144.0	15.4	171	163.0	13.7
210	197.1	25.2	144	191.7	22.0
178	247.8	33.0	115	227.1	27.7
145	294.0	40.6	85	265.0	37.0
111	334.1	50.3	50	308.5	45.4
73	392.3	60.6	0	368.1	60.3
30	460.5	73.2			
0	525.0	83.5			
Calibration at 45.5°C			Calibration at 57.5°C		
260	134.3	9.0	229	264.6	34.3
226	169.3	17.0	198	311.8	43.5
119	199.0	23.7	170	352.3	56.8
172	220.9	31.3	152	442.5	67.4
138	269.4	37.8	93	528.3	81.2
99	316.3	46.9	45	601.5	92.4
60	356.9	54.6	0	677.8	103.2
34	404.4	63.2			
0	462.6	73.7	Calibration at 73.7°C		
			369	190.7	37.6
162	142.5	11.0	309	241.7	49.5
126	183.1	20.0	261	303.7	61.7
91	219.6	28.0	212	418.1	84.4
63	253.1	34.3	166	504.0	97.6
34	295.3	42.6	114	572.2	84.0
0	340.1	51.3	57	630.3	99.5
			0	726.8	111.7

TABLE VII

Calculation of Replaceable Capacitance of Cell

Temperature °K	$(\epsilon-1) \times 10^6$ Ammonia	ΔC	C_o
296.91	5062	2.012	344.59
	5062	2.007	344.54
309.91	5614	1.824	334.91
	5614	1.817	333.72
319.66	5315	1.752	329.55
	5315	1.743	328.03
330.66	4946	1.607	303.21
346.86	4523	1.550	344.35

TABLE VIII

Dielectric Constant Data For Isopropyl Ether

Pressure mm of Hg	Capacitance $\mu\mu f \times 10^2$	Pressure mm of Hg	Capacitance $\mu\mu f \times 10^2$
Measurements at 36.75°C		Measurements at 45.5°C	
184	15.8	124	16.6
158	18.9	110	20.5
133	22.9	93	25.0
113	26.0	79	29.9
82	42.2	62	34.4
58	45.9	38	41.3
25	61.0	22	46.4
0	71.0	0	54.0
123	34.2	175	14.8
100	40.0	157	20.0
84	44.2	138	24.6
58	51.2	121	29.0
26	61.0	103	34.8
0	71.7	81	40.0
		61	48.2
100	36.3	44	53.8
78	42.0	20	60.5
58	47.8	0	67.4
33	56.6		
0	67.9		
87	45.4		
69	49.8		
51	53.8		
34	57.9		
13	63.0		
0	67.0		

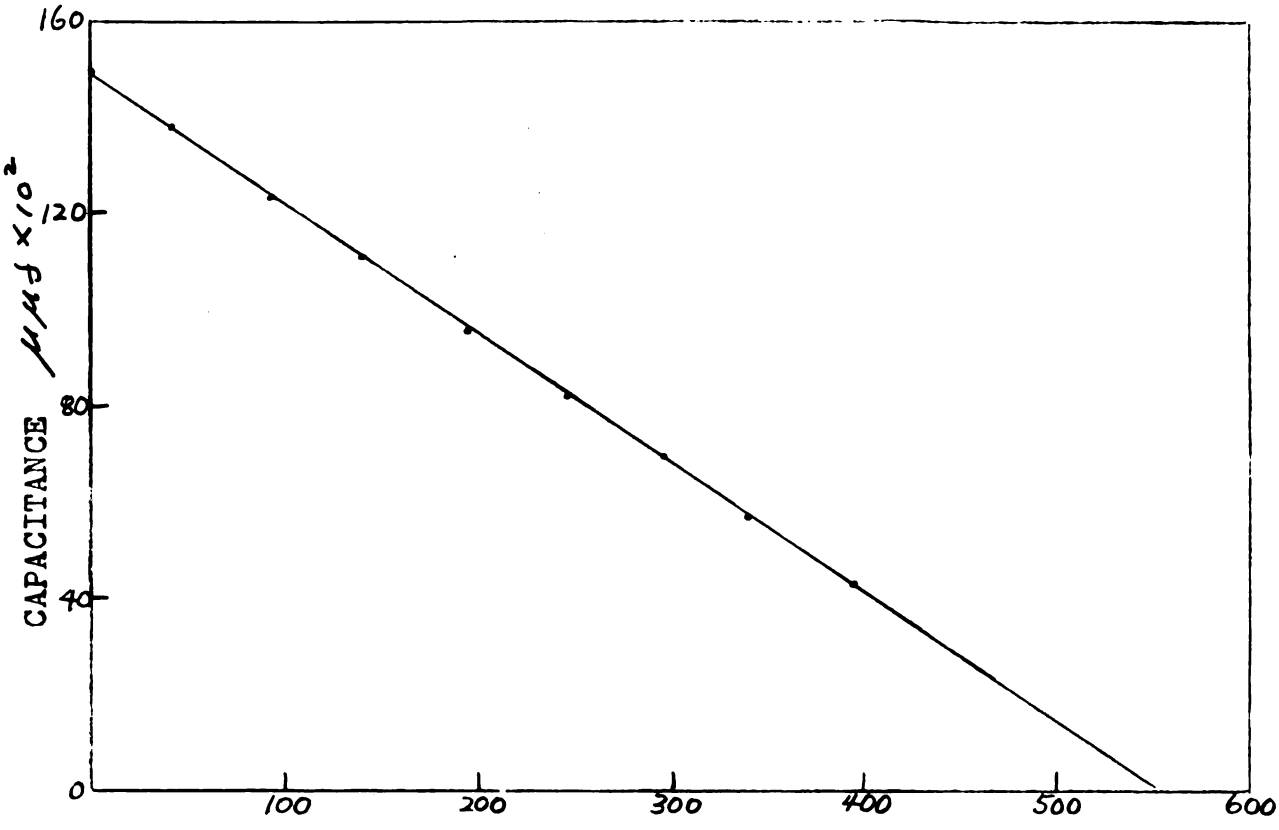

Figure V. Typical Plot of Cell Calibration Data-
Calibration of Cell at 23.75°C

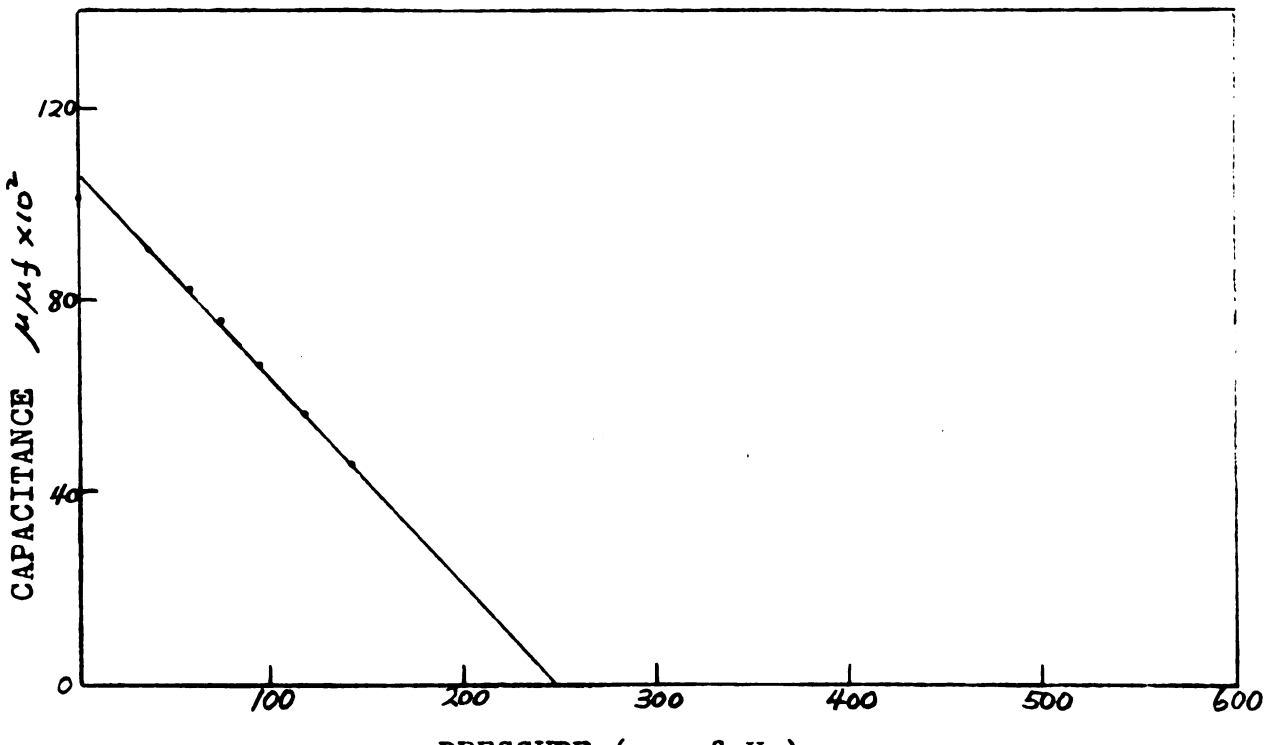

Figure VI. Typical Plot of Dielectric Constant Data-
Calculation of Isopropyl Ether at 23.75°C

TABLE IX

Dielectric Constant Data for tert-Butylamine

Pressure mm of Hg	Capacitance $\mu\mu f \times 10^2$	Pressure mm of Hg	Capacitance $\mu\mu f \times 10^2$
Measurements at 34.75°C		52	50.2
190	8.6	19	59.4
155	20.0	0	65.4
130	26.8		
102	34.8	102	29.7
71	43.4	91	33.2
32	55.0	64	36.8
0	65.0	36	44.1
		15	49.4
149	22.8	0	54.6
125	30.0		
100	37.0		
72	44.4		
45	53.0		
22	60.0		
0	67.4		
Measurements at 45.50°C			
183	15.4		
160	21.4		
142	26.3		
120	32.6		
95	39.8		
75	43.8		

TABLE X

Dielectric Constant Data for Trifluoroacetic Anhydride

Pressure mm of Hg	Capacitance $\mu\mu f \times 10^2$	Pressure mm of Hg	Capacitance $\mu\mu f \times 10^2$
Measurements at 23.75°C		Measurements at 36.75°C	
196	30.2	181	30.9
166	39.5	155	38.2
132	50.0	122	47.4
103	59.5	87	54.2
67	71.4	56	67.4
26	84.0	26	75.0
0	92.6	0	85.7
220	27.7	220	20.2
193	35.5	187	29.4
160	45.7	152	39.0
128	55.0	120	48.2
102	64.6	91	56.6
67	76.0	59	66.2
26	91.6	22	77.4
0	97.4	0	84.6
		Measurements at 45.5°C	
		244	4.3
151	50.0	209	13.0
127	57.3	177	21.4
95	67.7	140	31.2
60	78.4	105	40.8
26	88.6	71	50.8
0	97.0	35	65.2
		0	74.6
204	14.0		
170	23.4		
135	33.4		
99	43.2		
66	52.4		
26	65.4		
0	74.6		

TABLE V (Continued)

Pressure mm of Hg	Capacitance $\mu\mu f \times 10^2$	Pressure mm of Hg	Capacitance $\mu\mu f \times 10^2$
163	13.2		
132	21.7		
105	27.8		
79	36.2		
56	42.0		
22	51.8		
0	59.4		

TABLE VI

Dielectric Constant Data for Phosphorus Trichloride

Pressure mm of Hg	Capacitance $\mu\mu f \times 10^2$	Pressure mm of Hg	Capacitance $\mu\mu f \times 10^2$
Measurements at 57.5°C		104	57.2
116	51.7	85	59.8
103	53.3	67	63.8
97	54.4	47	67.7
82	56.2	32	71.0
72	57.8	15	74.2
64	60.5	0	76.0
44	63.8		
26	67.7		
12	70.5		
0	73.3		

TABLE XII

Dipole Moment Calculations by the Refractivity Method

Temperature °K	ΔC^* $\mu\mu f$	$(\epsilon-1)\times10^6$	V_M	P_M cc/mole	$(P_M-RD)_T$ cc/mole	μ D
Isopropyl Ether						
309.91	2.1509	6632	25428	56.09	7774.2	1.12
	2.1509	6632	25428	56.09	7774.2	1.12
	2.1033	6547	25428	55.28	7354.2	1.10
318.66	2.1655	6586	26146	57.29	8170.4	1.16
	2.0313	6190	26146	53.75	7042.4	1.08
tert-Butylamine						
309.91	2.170	6697	25428	56.62	10013.2	1.29
	2.156	6648	25428	56.22	9859.2	1.27
318.66	1.997	6075	26146	52.84	9001.4	1.22
	2.004	6096	26146	53.02	9148.7	1.23
Trifluoroacetic Anhydride						
296.91	2.4158	7014	24361	56.14	13360.9	1.43
	2.4013	6972	24361	56.43	13368.9	1.43
309.91	2.1160	6505	25428	55.18	13440.8	1.43
	2.1342	6581	25428	55.46	13589.6	1.49
318.66	2.1014	6301	26146	55.59	13950.9	1.51
	2.0900	6357	26146	55.30	13858.5	1.51
Phosphorus Trichloride						
330.61	1.4014	4096	27130	44.13	5272.0	0.98
	1.4013	4096	27130	44.13	5272.1	0.98

*Replaceable capacitance of cell

C_0 = 344.42 $\mu\mu f$ at 296.91°

C_0 = 324.31 $\mu\mu f$ at 309.91°

C_0 = 308.79 $\mu\mu f$ at 318.66°

C_0 = 303.21 $\mu\mu f$ at 330.66°

TABLE XIII

Average Dipole Moments in Vapor Phase

Substance	μ - Debye
Isopropyl ether	1.1?
tert-Butylamine	1.25
Trifluoroacetic anhydride	1.49
Phosphorus trichloride	0.93

CHAPTER VI

DISCUSSION

tert-Butylamine.[1] The dipole moment of t-butylamine was found to be 1.2[illegible] in the gas phase in this work; the value 1.3[illegible] has been reported in benzene solution ([illegible]). Probably a solvent effect causes the apparent moment in solution to be higher than the gas value. For the ammonia molecule, the moment value found (41) in benzene solution is 0.05 lower than the gas value 1.4[illegible]. In the aliphatic amines replacement of amino-hydrogen atoms by alkyl groups leads to a decrease in the moment. This may be due to the inductive effect of the methyl groups.

Trifluoroacetic Anhydride.[2] The dipole moment of trifluoroacetic anhydride was found to be 1.4[illegible]. The electric moment of acetic anhydride in the gas phase has been reported to be [illegible].7-[illegible] ([illegible]). The moment of the CF_3 group partially opposes the C=O and C-O group moments so the moment of trifluoroacetic anhydride is lower than that of acetic anhydride.

This low value of moment also rules out the possibility of a "chelate ring" in the acetyl group in which the oxygen atoms are made equivalent by resonance. The

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[1] [illegible]

[2] [illegible]

elimination of this chelate structure is confirmed by [illegible] and Brockway ([illegible]), who concluded that the two carbon-oxygen distances in acetic acid were quite different, one distance being identical with that in ketones, the other with that in alcohols. The electron diffraction results do not give any direct information because of the high scattering power of CF_3 group. They also indicated that the CF_3 group is free to rotate at large amplitudes.

Phosphorus trichloride[5] A dipole moment of 0.8[illegible] D was found for phosphorus trichloride. This is in good agreement with the value 1.0[illegible] D obtained by [illegible] and [illegible] ([illegible]) in benzene and in carbon tetrachloride. This indicates that the solvent effect is not large. It is probable that there is no [illegible] association.

The pyramidal configuration of three bonds formed by phosphorus has been demonstrated by electron diffraction studies of all four halides which have bond angles of about 100°. By using the following equation, the dipole moment can be obtained theoretically from the bond moments:

$$\mu = (m_1^2 + m_2^2 + 2m_1 m_2 \cos\theta)^{1/2} \qquad (24)$$

since $m_1 = m_2 = 0.81 D$

$$\therefore \mu = [(0.81)^2 + (0.81)^2 + 2(0.81)(0.81)\cos 100°]^{1/2}$$

$$= 1.58 D$$

---

[5] [illegible] Chemical Co., [illegible], Ohio.

The calculated value is higher than the value observed. This is probably due to some other effects, such as inductive effect or interactions between the bond dipoles in phosphorus trichloride.

Isopropyl Ether.[4] The dipole moment of isopropyl ether reported in this work is 1.13D. The isopropyl ether moment agrees very well with Smyth and Le Fevre's value (43), 1.13D in gas.

It is also interesting to know that the average of the moment of the symmetrical ethers (1.29D) is larger than that of the unsymmetrical ethers (1.17D). Symmetry in ethers might be expected to stabilize hyper conjugation structures which represent polarization of the alkyl group of oxygen.

Isopropyl ether probably has the H-C-O-C-H arrangement flat, with the hydrogen atoms close together. (ca. 1.7 A between centers). However this arrangement is sterically allowable. There is also probably some flexibility of the alkyl radicals.

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[4] From Eastman Organic Chemical Distillation Products Industries, Rochester 3, N.Y. Division of Eastman Kodak Co.

CHAPTER VII

SUMMARY

The electric moments of four compounds of oxygen, nitrogen and phosphorus have been measured in the vapor phase. The substances studied, and the electric moments found in this investigation, are: isopropyl ether 1.13D, tert-butylamine 1.25D, trifluoroacetic anhydride 1.40D, and phosphorus trichloride 0.98D. Only isopropyl ether had been studied in the vapor state previously and the value reported by Le Fevre, 1.13D, is in excellent agreement with the value reported here.

The electric moment of phosphorus trichloride found in this work in the vapor state may be compared with the values of 0.80D (54) and 0.90D (55) reported in the literature for phosphorus trichloride dissolved in carbon tetrachloride and benzene, respectively. Since the electric moments of most substances are 0.1-0.2D lower in solution than in the gas phase the behavior of phosphorus trichloride is normal. tert-Butylamine, however, has a lower moment in the vapor phase than the value 1.32D (44) found in benzene solution. This anomalous behavior has been reported in the literature for other amines; thus, triethylamine has a moment of 0.82D in the vapor state but 0.90D in benzene solution.

The electric moment of trifluoroacetic anhydride in the vapor state was found in this work, to be much lower than that reported in the literature for acetic anhydride (~ 2.8). The moment calculated for trifluoroacetic acid from bond moments is 1.4D assuming that the angle C-O-C is 110° and the angle O-C=O is 125° in the anhydride. Since the agreement between observed and calculated moments is so good the bond angles in trifluoroacetic anhydride are probably not far from the values assumed above.

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