Combining the above values for the three terms in (27)

$$\Delta S_h = \frac{R}{2}[\ln(2\pi\nu) + 1 - 1/3\nu - \ldots]\quad(28)$$

Equation (28) reduces to (26) when ν is replaced by $\overline{DP}_n$ and series terms of the order of $1/\nu$ or smaller are neglected.

Summary

The individual molecules of a linear polyester have only a temporary existence when heated to a suitable temperature, due to the occurrence of ester interchange between an ester group of one polymer molecule and the terminal functional group of another. While such processes have no effect on the number average degree of polymerization, they may modify the distribution of species.

Such considerations lead to the concept of an entropy of heterogeneity and of an equilibrium size distribution; the latter is identical with that obtained directly by random poly-condensation.

The transformation in the distribution of species in a mixture of polyesters has been observed by viscosity measurements. The results confirm the theoretical predictions.

The conversion of a cyclic ester (lactone) to a linear polyester should yield a much narrower distribution of species than is obtained by poly-condensation, but if ester interchange occurs between the polymer molecules subsequent to their initial formation, the distribution will be broadened.

Dipole Moments in the Vapor State and Resonance Effects in Some Substituted Benzenes

BY EVERETT C. HURDIS AND CHARLES P. SMYTH

The influence of resonance upon the dipole moment of a molecule containing a single polar group has been observed in both aromatic and unsaturated aliphatic molecules and the mutual effects of two polar groups in an aromatic molecule have been noted in a few cases, such as that of p-nitroaniline. In the case of two identical groups para to one another on the benzene ring, these mutual effects upon the dipole moments cancel each other and cannot, therefore, be detected, while in the ortho position, the mutual inductive effects of the two groups tend to obscure any effect of the resonance of one upon that of the other. It was hoped that, in spite of the smallness of the differences between the different carbon–halogen moments, accurate determinations in the vapor state of the moments of para-dihalogenated benzenes containing two different halogens might give quantitative evidence of the differences in resonance effects of the halogens. Unfortunately, the possibility of the presence of small quantities of the ortho-disubstituted benzenes as impurities in the samples of the para-compounds, which were too small for extensive purification, reduces the presumed accuracy of the results obtained for these compounds. Measurements upon iodobenzene and confirmation of moment values already in the literature for chloro- and bromobenzene were carried out to check the precision of the measurements and facilitate the interpretation of the results for the dihalogenated benzenes. Measurements were also made upon very pure samples of o-xylene and p-xylene with the object of observing possible small mutual induction or resonance effects of two adjacent methyl groups and of checking the group moment value to be assigned to a methyl group attached to a benzene ring.

Purification of Materials

Chlorobenzene.—Material from the Eastman Kodak Company was dried over calcium chloride and fractionally distilled; b. p. 130.5° (755 mm.).

Bromobenzene.—Material from the Eastman Kodak Company was dried over calcium chloride and fractionally distilled; b. p. 154.7° (753 mm.).

Iodobenzene, Sample I.—Material from the Paragon Testing Laboratories was fractionally distilled in a column of fourteen theoretical plates; b. p. 188.3° (762 mm.).

Iodobenzene, Sample II.—Iodobenzene was prepared by the method of "Organic Syntheses," Collective Volume I. p. 316, an all glass system being used. Fractionation gave 234 g. of material boiling between 188.2 and 188.5° (760 mm.). This was further distilled under low pressure, the main fraction (b. p. 98° at 37 mm.) being used for the measurements. The freezing point of this sample was measured by means of a platinum resistance thermometer

and found to be −31.8° ("International Critical Tables" gives −31.4°).

p-Fluorobromobenzene.—About twelve grams of material from the Eastman Kodak Company (n^{20}D 1.5279, $n^{21.8}$D, 1.5270) was sealed into a trap connected with the gas apparatus. For measurement, a simple fractionation was made by distilling the first 3 g. under vacuum into another trap, and the middle 6 g. into the U-tube from which vapor was introduced into the gas cell.

p-Fluoroiodobenzene.—Ten grams of material from the Eastman Kodak Company ($n^{21.8}$D 1.5794) was purified by vacuum distillation in the gas apparatus directly before each measurement, as in the case of the *p*-fluorobromo compound.

p-Fluoronitrobenzene.—Material from the Eastman Kodak Company ($n^{23.6}$D 1.5304, n^{25}D 1.5294) was purified by vacuum distillation by the method used for the two dihalogenated benzenes.

o-Dichlorobenzene.—A special 99.4% grade of material kindly given us by the Heyden Chemical Corporation was used without further purification; b. p. 180.3° (750 mm.); m. p. −17.1°; n^{25}D 1.5486; n^{20}D 1.5513. "International Critical Tables" gives normal boiling point 179°, melting point −17.6°, n^{20}D 1.549.

o- and *p*-Xylene.—The hydrocarbons used in this work were supplied as a part of the American Petroleum Institute Pure Hydrocarbon Program. They were prepared and purified at the Pure Hydrocarbon Laboratory, Department of Chemistry, operating as project No. 31 of the Ohio State University Research Foundation. A full description of these products will be published at a later date.

Experimental Results

The dielectric constants of the vapors were measured with the apparatus and, essentially, the same technique that has been previously described.[1] A polarization value, *P*, was obtained at an absolute temperature, *T*, by measurements over a wide range of pressure. The value of *P* given by each such run is shown in Table I, as is also the corresponding value of the dipole moment μ calculated as $\mu = 1.281 \times 10^{-20}[(P - MR\mathrm{D})T]^{1/2}$. For the dihalogenated benzenes, many of the values represent the averages of two or more runs. The molar refraction for the sodium *D* line, $MR\mathrm{D}$, is listed for each compound in Table II together with the average of the moment values in Table I. The moment of fluorobenzene, which is included in Table II for purposes of comparison, has been recalculated from previous measurements,[2] by the use of $MR\mathrm{D}$ instead of the total induced polarization given by temperature dependence without consequent alteration in value. The few measurements on chloro- and bromobenzene were run primarily as a check upon the absolute accuracy of the determinations. The

(1) Wiswall and Smyth. *J. Chem. Phys.*, **9**, 352 (1941).
(2) McAlpine and Smyth. *ibid.*, **3**, 55 (1935).

polarization values for chlorobenzene, 72.2 and 72.3 at 436.1°K., are in excellent agreement with

TABLE I

DIPOLE MOMENTS AND DEPENDENCE OF POLARIZATION UPON TEMPERATURE

T, °K.	*P*	$\mu(\times 10^{18})$
	Chlorobenzene	
435.8	73.1	1.73
436.1	72.2	1.72
436.1	72.3	1.72
	Bromobenzene	
455.8	75.8	1.77
455.8	75.7	1.77
	Iodobenzene (Sample I)	
476.1	78.2	1.75
476.1	79.7	1.78
495.4	76.8	1.75
495.4	75.5	1.72
495.4	72.6	1.65
495.4	76.5	1.74
508.3	74.8	1.73
523.2	75.2	1.76
	Iodobenzene (Sample II)	
433.0	77.1	1.64
433.0	78.5	1.67
433.0	80.0	1.70
458.9	75.0	1.64
463.1	72.9	1.60
463.1	79.3	1.75
472.3	74.6	1.66
473.0	74.4	1.66
487.1	75.2	1.70
487.1	76.0	1.71
	p-Fluorobromobenzene	
436.1	37.4	0.51
444.1	37.6	.53
449.0	37.8	.55
454.7	37.4	.53
461.6	37.3	.52
490.5	37.1	.52
523.9	37.4	.57
	p-Fluoroiodobenzene	
470.1	49.4	0.89
492.4	49.1	.89
	p-Fluoronitrobenzene	
487.9	135.1	2.865
499.4	132.3	2.86
509.3	131.0	2.87
523.7	128.2	2.87
	o-Dichlorobenzene	
444.9	122.3	2.51
473.3	117.5	2.52
493.1	114.4	2.52
	113.7	2.50
	113.7	2.50
507.6	111.6	2.51
522.7	109.4	2.51

TABLE I (*Concluded*)

T. °K.	P	$\mu(\times 10^{18})$

p-Xylene (A. P. I. Hydrocarbon Laboratory, Manifest No. 15-P)

447.4	37.7	(0)
447.4	37.7	(0)
447.4	37.6	(0)

o-Xylene (A. P. I. Hydrocarbon Laboratory, Manifest No. 13-P)

412.5	(43.7)	(0.65)
433.1	43.2	.63
462.1	42.8	.62
497.3	42.3	.61
512.1	42.2	.62

TABLE II

MOLAR REFRACTIONS AND AVERAGE MOMENT VALUES

	MRD	$\mu(\times 10^{18})$
Fluorobenzene	26.0[a]	1.57
Chlorobenzene	31.1[b]	1.72
Bromobenzene	34.0[b]	1.77
Iodobenzene	39.2[b]	1.70
p-Fluorobromobenzene	33.7[c]	0.5
p-Fluoroiodobenzene	39.2[c]	.9
p-Fluoronitrobenzene	32.4[e]	2.87
p-Xylene	36.0[d]	(0)
o-Xylene	35.8[d]	0.62
o-Dichlorobenzene	36.0[e]	2.51

[a] Calculated from data in "International Critical Tables." [b] Landolt–Börnstein (5th ed.). [c] Measured in this Laboratory. [d] Calculated from data furnished by Professor C. E. Boord. [e] Calculated from refractions in Landolt–Börnstein (5th ed.).

the value 72.5 obtained from the data of McAlpine and Smyth[2] by interpolation at this temperature and the values for bromobenzene, 75.8 and 75.7 at 455.8°K. are indistinguishable from the value 75.8 obtained from the data of Groves and Sugden[3] by interpolation. The moment values calculated from these polarizations are slightly higher, 0.02 for chlorobenzene and 0.06 for bromobenzene, than the values obtained in the earlier work by the use of total induced polarization instead of molar refraction. This neglect of the small atomic polarization which may cause the total induced polarization to be slightly higher than *M*RD, is evidently unimportant in the case of the monohalogenated benzenes, but is serious in that of the *p*-dihalogenated benzenes. In view of the symmetry of the *p*-xylene molecule, its moment may safely be assumed to be zero. Its polarization was measured only in order to obtain a total induced polarization value, which, as a fair approximation, could be taken equal to that of *o*-xylene and thus used, instead of the *M*RD value, to calculate the dependable value for the latter

(3) Groves and Sugden, J. Chem. Soc., 971 (1935).

compound in Table II. The difference of 0.2 in the *M*RD values for the two compounds indicates that the total polarization of *p*-xylene may differ by a few tenths of a unit from the induced polarization of *o*-xylene. Decomposition of the iodobenzene limits the range of temperature over which the measurements may be made and, probably, causes the unusually large variation in the moment value for it in Table I. The two samples of satisfactory purity give mean moment values differing by 0.07 from each other. The average of these two in Table II is from 0.10 to 0.15 higher than the value to be expected for the vapor on the basis of the values obtained from solution measurements.[4,5] In view of this, the value 1.70 may be high, but it is, probably, less than 0.1 high.

Discussion of Results

It happens that the chloro-, bromo- and iodobenzene moment values in Table II have almost the same differences from one another as the corresponding butyl halides.[6] The fluorobenzene moment is lower than that of chlorobenzene, as the alkyl fluoride moment is lower than that of the alkyl chloride.[7] The slight increases in the values of the bromobenzene and iodobenzene moments lessen the calculated reduction in moment by contributions from structures with double-bonded positive halogens and, hence, show the amounts of double bond character in the C–Cl, C–Br, and C–I bonds to be more nearly equal than previously supposed.[6]

The moment value of *p*-fluorobromobenzene in Table II is 0.3 higher than the difference between the moments of fluoro- and bromobenzene, to which it should be equal in the absence of complicating factors. The presence of a small amount of *o*-fluorobromobenzene as an impurity together with a larger atomic polarization than is assumed in the use of *M*RD as the total induced polarization could account for this discrepancy, which is, however, a little large to arise from these causes. The moment value for *p*-fluoroiodobenzene is 0.8 higher than the small difference 0.1 between the moments of fluorobenzene and iodobenzene. It would require about 10% of *o*-fluoroiodobenzene present as an impurity to account for this discrepancy, or, at least, 5% of the ortho compound plus an abnormally high atomic polarization

(4) Parts, Z. physik. Chem., B10, 264 (1930).

(5) Tiganik, ibid., B13, 425 (1931).

(6) Smyth, THIS JOURNAL, 63, 57 (1941).

(7) Smyth and McAlpine, J. Chem. Phys., 2, 499 (1934).

value, both of which possibilities are somewhat remote. The larger moment of the p-fluoroiodobenzene seems to correspond to the fact that the electronegativity difference between fluorine and iodine is greater than that between fluorine and bromine, the difference between the two moments coinciding with the I-Br bond moment, 0.4.[8] The moments of the two compounds could be accounted for by writing for their molecules, in addition to their normal covalent structures and their quinoid structures of the type

, ionic structures such as
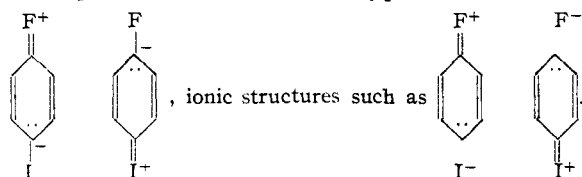
The much greater electronegativity of the fluorine would make the ionic structure with negative fluorine predominate over that with negative iodine or bromine, giving a moment opposite in direction to that to be expected from the small differences between the moments of the monosubstituted benzenes. These combinations of structures should lead to small moments of the order of magnitude of those observed and differing in value according to the electronegativity differences as observed.

In order to obtain a moment value for nitrobenzene directly comparable with the values in Table II, the previous data[2] were recalculated with MR_D instead of the total induced polarization. The difference between the moment value, 4.25, thus obtained and the moment of fluorobenzene in Table II gives a value 2.68 for p-fluoronitrobenzene, 0.19 lower than the observed value in Table II. Although part of this difference could arise from the presence of o-fluoronitrobenzene as an impurity in the para compound, it has been previously pointed out[9] that the moment of p-chloronitrobenzene, 2.78, measured[10] for the vapor of a carefully purified sample is high, probably because of contributions from highly polar structures such as
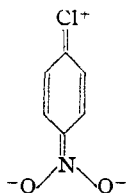
(8) Smyth, *J. Phys. Chem.*, **41**, 209 (1937).
(9) Smyth and Lewis, THIS JOURNAL. **62**, 721 (1940).
(10) Groves and Sugden. *J. Chem. Soc.*, 1782 (1937).

The elevation, 0.25, of the moment above the calculated value, 2.53, is slightly larger than that in the case of p-fluoronitrobenzene, 0.19, which, because of possible impurity, represents an upper limit for the elevation. It appears that, in the case of these two compounds, the presence of the nitro group effects a greater increase in the amount of double bond character in the C–Cl than in the C–F bond.

The polarization of the p-xylene vapor in Table I is 0.6 higher than the value 37.07 found for the same sample in the liquid state at 293.1°K. by Dr. P. F. Oesper, a difference of the magnitude and direction normally found between liquid and vapor values. The absence of error due to impurity and to neglect of atomic polarization should make the moment value of o-xylene in Table II extremely accurate. It differs by only 0.01 from the value previously used for the moment of two o-methyl groups[9] and the natural assumption of an angle of 60° between the two group moments leads to a calculated value 0.36 for the group moment of methyl on a benzene ring in excellent agreement with the moment of toluene, 0.35,[11] on which the above-mentioned value for the two o-methyl groups was based. The excellence of this agreement shows, in harmony with previous conclusions, that any mutual inductive or resonance effects between the two ortho-methyl groups are too small to detect by means of dipole moments. It may be mentioned that the use of MR_D instead of the p-xylene polarization in calculating the o-xylene moment would give a value 0.73 instead of 0.62 and 0.42, instead of 0.36, for the methyl–benzene group moment. Similar use of MR_D instead of the total induced polarization for toluene would give a moment value 0.45 instead of 0.35. This does not mean, however, that the group moment value 0.42 or 0.45 should be used for consistency in calculating the moments of more polar molecules, for which MR_D values have been used in obtaining the moment from the experimental data, since large moment values are little affected by neglect of atomic polarization. The value 0.36 is, therefore, to be regarded as correct for the group moment produced by the attachment of a methyl group to a benzene ring.

The moment of o-dichlorobenzene was measured because of the fact that the value, 2.16, obtained by Groves and Sugden[10] from vapor meas-

(11) McAlpine and Smyth. THIS JOURNAL. **55**, 453 (1933).

urements was 0.1 lower than the value found by several investigators from measurements in solution, although the solvent effect, which, in the case of chlorobenzene, lowers the solution value to such an extent that the gas value is 10% higher than that measured in solution, should lead to a similarly lower value for o-dichlorobenzene.[6] Since addition of 10% to the solution value, 2.27, for o-dichlorobenzene gives a value, 2.50, practically identical with the newly determined gas value, 2.51, in Table II, it is evident that there is no anomaly in the solvent effect for this compound.

The writers wish to express their thanks to Professor C. E. Boord of Ohio State University and Dr. George Calingaert of the Ethyl Gasoline Corporation for the xylenes and to Dr. P. D. Hammond of the Heyden Chemical Corporation for the o-dichlorobenzene used in this investigation.

Summary

The dielectric constants of the vapors of chloro-, bromo-, iodo-, p-fluorobromo-, p-fluoroiodo-, p-fluoronitro- and o-dichlorobenzene, and of p- and o-xylene have been measured and used to calculate the dipole moments of the molecules. The moment values found for chlorobenzene and bromobenzene agree closely with those in the literature, while that for iodobenzene is slightly higher than would be expected on the basis of previous measurements in solution. The moment value of o-dichlorobenzene is much higher than the one in the literature and in excellent agreement with that obtained by correcting the solution value for solvent effect. The data for the two xylenes give an accurate value, 0.36, for the group moment produced by the attachment of a methyl group to a benzene ring. The moments found for the p-disubstituted benzenes are larger than the differences between the corresponding mono-substituted compounds by amounts which may be accounted for by resonance.

PRINCETON, NEW JERSEY

Condensation Products of Ketene with Ketones[1]

By B. H. Gwynn with Ed. F. Degering

The reactions of ketene have been studied rather extensively. It has been found to act as the anhydride of acetic acid. Although it is commonly prepared from acetone and therefore contaminated with it to some extent, no one appears to have noted a reaction between the two. Investigations have been reported in which the reactivity of ketene with ketones was studied without a catalyst[2] and in the presence of anhydrous sodium or potassium acetate.[3] No reaction was noted. Acetone has been used as a solvent in the acid catalyzed acetylation of carbohydrates[4] with ketene. A reaction undoubtedly took place in these cases but escaped notice. Similarly, in the acid catalyzed acetylation of butyl alcohol,[5] the ketene was contaminated with acetone, and the two probably reacted to a limited extent.

This investigation has shown that ketene does react with ketones. In the presence of a small amount of sulfuric acid the product is the acetate of the enol form of the ketone, as indicated by the equation

$$H_2C:C:O + H \cdot O \cdot C(CH_3):CH_2 \; (\rightleftarrows CH_3 \cdot CO \cdot CH_3 /$$
$$H_2SO_4) \longrightarrow CH_3 \cdot CO \cdot O \cdot C(CH_3):CH_2$$

Since the completion of this work, ketene has been reported to react with vinyl ketones to yield cyclic esters of the enol form of delta keto acids,[6] an entirely different type of reaction from that observed in this study, as indicated

$$H_2C=C=O + H_2C=CH-CO-CH_3 \longrightarrow CH_3C \underset{HC}{\overset{O}{\diagup}} \underset{\diagdown CH_2}{\overset{C=O}{\diagdown}}$$
$$HCH$$
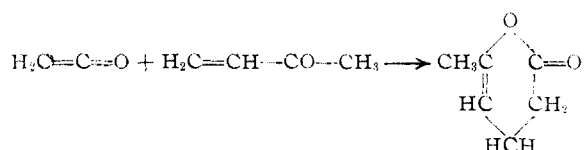
Experimental Part

Apparatus.—Ketene was generated in a lamp which was constructed in the same manner as one described by Hurd.[7] In order to separate acetone from the ketene, the

(1) Abstract of a thesis by B. H. Gwynn, submitted to the faculty of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry, June, 1942. Present address, Westvaco Chlorine Products Corp., Carteret, New Jersey.
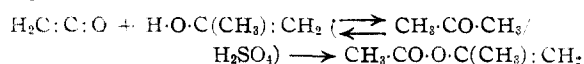
(2) Staudinger and Klever, Ber., 41, 594 (1908).

(3) Hurd and Williams, THIS JOURNAL, 58, 962 (1936).

(4) Hurd, Cantor and Roe, ibid., 61, 426 (1939).

(5) Morey, Ind. Eng. Chem., 31, 1129 (1939).

(6) U. S. Patent 2,265,165, Dec. 9, 1941; C. A., 36, 1614 (1942).

(7) Hurd, J. Org. Chem., 5, 122 (1940).