

## The Dipole Moments of Certain Monosubstituted Benzenes in the Vapor State

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enter the benzene nucleus more rapidly than the second molecule of  $H_2$ , which in turn would enter more rapidly than the first molecule. If this same relative order of activation energies held for the surface reactions one would also expect cyclohexane to be the product obtained upon catalytically hydrogenating benzene. This is apparently the case, although the surface reaction mechanism may be such that the separate steps are indistinguishable.<sup>15</sup>

The activation energies calculated for the reactions involving Ni are probably not very

precise, but it is undoubtedly of significance that they are all of a lower order of magnitude than that for the hydrogenation of benzene. Thus, one might expect that, at least insofar as the rates of adsorption and desorption of  $H_2$  and benzene on it are rate-determining, the hydrogenation of benzene could be achieved more easily on a catalytic nickel surface. This is experimentally the case, as was shown by Sabatier<sup>16</sup> and studied in detail by Dougherty and Taylor.<sup>17</sup> The latter authors found the catalytic reaction to be rapid from 60°C to 200°C.

<sup>15</sup> For example, see Ballandin, *Zeits. f. physik. Chemie* **B2**, 289 (1929).

<sup>16</sup> Sabatier, *Ind. Eng. Chem.* **18**, 1006 (1926).

<sup>17</sup> Dougherty and Taylor, *J. Phys. Chem.* **27**, 533 (1923).

## The Dipole Moments of Certain Monosubstituted Benzenes in the Vapor State

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The dielectric constants of the vapors of three monosubstituted benzenes have been determined over a range of temperature and used to calculate dipole moments as follows: fluorobenzene,  $1.57 \times 10^{-18}$ ; chlorobenzene,  $1.70 \times 10^{-18}$ ; nitrobenzene,  $4.19 \times 10^{-18}$ . These values are considerably higher than those found from previous measurements in solution and agree well with values calculated for the vapor state by the application of an empirical equation developed by Müller to measurements in solution.

THESE measurements were made nearly two years ago in an attempt to obtain reliable values for the moments of certain common dipoles which are frequently used in studies of molecular structure. They have taken on added interest because of recent work upon the dependence of the apparent value of a moment measured in solution upon the dielectric constant of the solvent.

The dielectric constants were measured with the apparatus previously described.<sup>1</sup> For fluorobenzene and chlorobenzene, the polarization  $P$  was calculated from the dielectric constant  $\epsilon$  and the molar volume  $V$  as  $P = [(\epsilon - 1)/(\epsilon + 2)]V$ , the polarization-pressure curve at each absolute temperature  $T$  being extrapolated to zero pressure to obtain a value  $P_0$  for use in the Debye equation,  $P = a + b/T$ . The value of the atomic

polarization was calculated as  $P_A = a - P_E$ , the difference between  $a$ , the total induced polarization, and  $P_E$ , the molar refraction extrapolated to infinite wavelength. The dipole moments were calculated from the values of  $b$  as  $\mu = 0.01273 \times 10^{-18}(b^{1/2})$  and should be in error by no more than  $0.01 \times 10^{-18}$ .

The same procedure in the case of nitrobenzene, which had to be measured at lower pressures than the other two substances gave a value  $4.03 \times 10^{-18}$  and the abnormally large value 20.5 for the atomic polarization. When the moment was calculated at each temperature by subtracting  $P_E$  from the total polarization at zero pressure, values were obtained which rose from 4.20 to  $4.25 \times 10^{-18}$  with rising temperature. As it appeared probable that greater errors arose from extrapolating to zero pressure the polarizations at pressures below 200 mm than from deviations from the gas laws, the polarizations

<sup>1</sup> McAlpine and Smyth, *J. Am. Chem. Soc.* **55**, 453 (1933); *J. Chem. Phys.* **2**, 499 (1934).

for nitrobenzene were taken as the averages of from four to nine values at each temperature. These average values are listed under  $P_0$  in Table I since they must differ by an almost negligible amount from the values at zero pressure. The probable error in the moment obtained for nitrobenzene is about  $0.05 \times 10^{-18}$ . The  $P_0$  values are used to obtain the values of  $a$  and  $b$  in Table II.

TABLE I. Polarizations.

Fluorobenzene		Chlorobenzene		Nitrobenzene	
$T, ^\circ\text{K}$	$P_0$	$T, ^\circ\text{K}$	$P_0$	$T, ^\circ\text{K}$	$P_0$
343.6	69.9	373.6	79.6	442.1	282.6
371.4	66.8	403.7	75.7	442.3	281.7
414.1	62.5	429.8	73.1	483.0	262.0
453.2	59.3	476.1	69.0	504.2	251.2
507.0	55.8	518.4	66.2	539.1	239.3
				548.7	234.0

TABLE II. Values of calculated constants.

	$a$	$P_E$	$P_A$	$b$	$\mu \times 10^{18}$
$\text{C}_6\text{H}_5\text{F}$	25.8	24.8	1.0	15190	1.57
$\text{C}_6\text{H}_5\text{Cl}$	31.7	29.9	1.8	17830	1.70
$\text{C}_6\text{H}_5\text{NO}_2$	37.7	31.6	6	108100	4.19

## PURIFICATION OF MATERIALS

### Fluorobenzene

Material from the Eastman Kodak Company was dried over calcium chloride and fractionated: b.p.,  $84.1^\circ$  (750 mm);  $n_D^{20}$ , 1.46593.

### Chlorobenzene

Material from the Eastman Kodak Company was shaken with concentrated sulfuric acid until the acid layer no longer became colored. It was then washed with water, with dilute potassium bicarbonate solution, and again with water, was dried over calcium chloride and distilled; b.p.,  $131.1^\circ$ ;  $n_D^{20}$ , 1.52459. A thorough drying of the material over phosphorus pentoxide and subsequent distillation gave a product with the same refractive index and a boiling point of  $130.7^\circ$  at 755 mm.

### Nitrobenzene

Merck's material was crystallized five times from its own melt, dried over phosphorus pentoxide, and distilled under reduced pressure; freezing point,  $5.71$ – $5.53^\circ$ ;  $n_D^{20}$ , 1.55257.

## DISCUSSION OF RESULTS

The atomic polarization values found for fluorobenzene and chlorobenzene are slightly smaller than those usually found for polar molecules of this size<sup>2</sup> and that for nitrobenzene a little larger, but, in view of the large error necessarily accumulated in these quantities, particularly, in the value for nitrobenzene, the differences are not significant.

When the value 1.57 was obtained for the moment of fluorobenzene, it seemed surprisingly high in comparison with the values 1.39<sup>3</sup> and 1.45<sup>4</sup> previously found in benzene solution. The value 1.70 then found for chlorobenzene vapor was higher by a corresponding amount than the results of the more accurate determinations among the many which had been made in solution.<sup>5</sup> The precise determinations of Müller<sup>6</sup> upon very dilute solutions then showed that the apparent dipole moment of a molecule increased with decreasing dielectric constant of the surrounding solvent. The part of the polarization given by  $P_E$  is practically independent of solvent,<sup>7</sup> but the orientation polarization  $P_M$  due to the permanent dipole in the molecule is given, according to Müller, by the empirical equation,  $P_{M \text{ gas}} = P_{M \text{ sol.}} / [1 - 0.075(\epsilon - 1)^2]$ , where  $\epsilon$  is the dielectric constant of the solvent in which the orientation polarization at infinite dilution,  $P_{M \text{ sol.}}$ , is determined. A similar equation gives the moment in the vapor state as  $\mu_{\text{gas}} = \mu_{\text{sol.}} / [1 - 0.038(\epsilon - 1)^2]$ , no correction for atomic polarization being made in  $P_{M \text{ sol.}}$  and  $\mu_{\text{sol.}}$ . Although the polarization and moment values of the vapors of chlorobenzene and nitrobenzene were unknown to Müller, he showed that these equations represented their variations with solvent. Application of the second equation to the results of Bergmann and of Nukada gives a calculated value 1.55 for the moment of fluorobenzene in the vapor state in excellent

<sup>2</sup> C. P. Smyth, J. Chem. Phys. **1**, 247 (1933).

<sup>3</sup> P. Walden and O. Werner, Zeits. f. physik. Chemie **B2**, 10 (1929).

<sup>4</sup> E. Bergmann, L. Engel and S. Sandor, ibid. **B10**, 106 (1930); A. Nukada, Nip. Chem. **5**, 41 (1932).

<sup>5</sup> Cf. Trans. Faraday Soc., Appendix, September (1934).

<sup>6</sup> H. Müller, Phys. Zeits. **34**, 689 (1933).

<sup>7</sup> C. P. Smyth, E. W. Engel and E. B. Wilson, Jr., J. Am. Chem. Soc. **51**, 1736 (1929).

agreement with the observed value in Table II. As these equations take no account of the atomic polarization, for which Walden and Werner make an arbitrary correction in the calculation of the moment, the first empirical equation is applied to Walden and Werner's value for the total polarization minus a value 25 for  $P_E$ . The value  $\mu_{gas} = 1.54$  is thus obtained. Application of the first empirical equation to Müller's determinations of the polarization of chlorobenzene in nine different solvents and calculation of the moment from the resulting  $P_{M, gas}$  values give moment values for the vapor state running from 1.62 to 1.67 with a mean value 1.65, slightly lower than the observed value 1.70 in Table II, which is in excellent agreement with the value 1.69 recently published by Groves and Sugden<sup>8</sup> for the vapor. A similar calculation from Müller's results on nitrobenzene in various solvents gives 4.18, 4.21 and 4.22 for the values obtained from solutions in hexane, carbon tetrachloride and benzene, respectively, and 4.29 and 4.37 from dekaline and carbon bisulfide. Calculations from the results of Jenkins<sup>9</sup> give 4.14 from the dekaline solutions at 25° and 4.09 at 142.4° and 4.06 from carbon bisulfide solutions. The mean of the results from the data of the two investigators for each substance happens to be close to the values found from the work of both investigators on other solvents. Jenkins' measurements in chloroform solution, however, give a calculated value of 6.84 for the nitrobenzene moment in the gaseous state indicating either that the solvent has some specific action on the

solute in this case or that the empirical equation cannot be relied upon when markedly polar solvents are used. The mean obtained from Müller's measurements in hexane, carbon tetrachloride and benzene is 4.20 and that from Jenkins' measurements in the same solvents and in cyclohexane is 4.18 in excellent agreement with the observed value 4.19 in Table II, which is in satisfactory agreement with the experimental value 4.23 recently published by Groves and Sugden.<sup>8</sup>

It is evident that, in the case of the three substances here studied, the empirical relation found by Müller between the apparent polarization and dipole moment of a substance in solution and the dielectric constant of the solvent serves admirably to calculate the moment in the vapor state. This added experimental evidence of the marked difference in some cases between the moment of the vapor and the apparent moment in solution emphasizes the need of considering the conditions under which moment values are determined before conclusions may be drawn from small differences in value. For instance, the difference in moment between chlorobenzene and methyl chloride<sup>10</sup> is only 0.16, while early work used a solution value for chlorobenzene to assign a value 0.4 to the difference. Since, however, most comparisons have been based upon measurements in the same solvent or in solvents differing by no great amount in dielectric constant, few, if any, of the accepted conclusions can be regarded as invalidated by this recent development.

<sup>8</sup> L. G. Groves and S. Sugden, *J. Chem. Soc.* 1094 (1934).

<sup>9</sup> H. O. Jenkins, *Nature* 133, 106 (1934); *Trans. Faraday Soc.* 30, 739 (1934).

<sup>10</sup> R. Sängner, *Helv. Phys. Acta* 3, 161 (1930); O. Fuchs, *Zeits. f. Physik* 63, 824 (1930).