thermal data. Even if the equilibrium data were extremely accurate they would not permit one to predict greater reliability for any particular datum because each equation involves a combination of several data. Equation D must, therefore, be regarded largely as an empirical equation which best represents the experimental points.

It should also be noted that none of the catalysts used was specific for the reaction in question, and hence side reactions such as the formation of methane or higher alcohols may have affected the values obtained. It would appear impossible to obtain closer agreement among the measured values of the equilibrium constant until a much more specific catalyst is found.

Summary

The equilibrium $CO + 2H_2 \rightleftharpoons CH_3OH$ has been investigated at temperatures of 225, 250 and 275° at a pressure of three atmospheres. The values obtained agree with the following theoretical equation, which is based on some of the most reliable thermal data available

$$\log_{10} Kp_0 = 3724/T - 9.1293 \log_{10} T + 0.00308\, T + 13.412$$

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

The Dipole Moments of Some Mono Substitution Products of Mesitylene

BY FRANCES BROWN, J. M. A. DE BRUYNE AND PAUL GROSS

Mesitylene compounds with substituents in the ring afford an unusual opportunity for studying the effects of the interaction of methyl groups with other substituents as reflected in the dipole moment values. The inherent moments due to the three methyl groups because of their symmetrical location in the ring cancel each other and allow of a study of the interactions between the methyl groups and the other substituent which is fairly free of the complicating factors usually present in molecules of this complexity. This paper gives the results of the measurements of the dipole moments of fluoro-, chloro-, bromo- and iodomesitylene and of nitromesitylene and mesitol.

Method and Apparatus.—Details of the experimental procedure and apparatus used will be found in previous papers.[1,2]

Materials.—The benzene and carbon tetrachloride used as solvents were purified as previously described.[1a]

Fluoromesitylene.—Mesityldiazonium borofluoride was prepared from mesidine hydrochloride by the method of Wilke-Dörfurt and Balz[3] and then decomposed by heating according to the procedure of Balz and Schiemann[4] to give fluoromesitylene which was purified by distillation, washing with sodium hydroxide, drying and refractionating four times. A sample with b. p. 168.5–168.7° was used.

Chloromesitylene was made by direct chlorination using a modification of the method of Fittig and Hoogewerff.[5] Chlorine and mesitylene were brought together at the lower end of a narrow inclined glass tube surrounded with cold brine, the gas bubbles carrying the mixture of chloromesitylene and mesitylene over into a trap filled with 5% sodium thiosulfate solution to prevent further reaction. The mixture separated from this was washed with 15% sodium hydroxide solution to remove residual acid and hydrolyze any side chain derivatives and then was washed with water, dried and distilled. The purified fraction used boiled from 103.6 to 103.7° at 25 mm.

Bromomesitylene was prepared by the method of Smith.[6] A sample with b. p. 119.2–119.3° at 25 mm. was used for the measurements.

Iodomesitylene.—This was prepared by the method of Datta and Chatterjee,[7] washed with 15% sodium hydroxide, with water, with sodium thiosulfate, followed by repeated recrystallization from alcohol giving a product which froze at 30.0°.

Nitromesitylene.—This was prepared by the method of Bamberger and Rising[8] with slight modifications and was purified by recrystallization from alcohol and by fractional crystallization; f. p. 43.0–43.2°.

Mesitol.—Mesidine hydrochloride was diazotized and the diazonium compound hydrolyzed in the usual manner to mesitol. The sample was recrystallized twice from petroleum ether; f. p. 71.5–71.8°.

Results.—In Table I are given the results of the density and refractive index measurements on the halogen substituted mesitylenes all of which could be measured as liquids at 30°. The last column gives the calculated molecular refractivity for the sodium D line. This information is not in the literature and so is included here.

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[1] (a) de Bruyne, Davis and Gross, THIS JOURNAL, **55**, 3936 (1933); (b) *Physik. Z.*, **33**, 719 (1932).

[2] Gross, *ibid.*, **32**, 587 (1931).

[3] Wilke-Dörfurt and Balz, *Ber.*, **60**, 115 (1927).

[4] Balz and Schiemann, *Ber.*, **60**, 1186 (1927).

[5] Fittig and Hoogewerff, *Ann.*, **150**, 323 (1869).

[6] Smith, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1931, Vol. XI, p. 24.

[7] Datta and Chatterjee, THIS JOURNAL, **39**, 438 (1917).

[8] Bamberger and Rising, *Ber.*, **33**, 3625 (1901).

TABLE I

Mesitylene	d^{30}	$n^{30}_{H\alpha}$	$n^{30}_{Na_D}$	$n^{30}_{H\beta}$	MR^{30}_D
Fluoro-	0.9694	1.47560	1.47949	1.48946	40.43
Chloro-	1.0337	1.51685	1.52119	1.53246	45.54
Bromo-	1.3116	1.54310	1.54802	1.56043	48.25
Iodo-	1.5588	1.58480	1.59073	1.60611	53.32

The results of the measurements on the solutions are given in Table II. The symbols have their customary significance.[1a]

Table III gives the values of the molar polarizations (P_2^∞) at infinite dilution, the molecular refractivities (R_2), and the dipole moments (μ) calculated from them by the Debye theory[1a] for the determination of dipole moments from solution measurements. The dipole moment of only one of these compounds has been previously reported. This is nitromesitylene for which Hammick, New and Williams[9] have recently reported a value of $\mu = 3.67\ D$[10] in benzene as solvent, in excellent agreement with that found here ($\mu = 3.65\ D$). Data for fluorobenzene are included also in Tables II and III. These measurements were carried out on a carefully purified sample by Miss Mary Gorman in this Laboratory. They were made because of the difference between the two existing values for fluorobenzene; that of Walden and Werner[11] ($\mu = 1.39\ D$) and that of Bergmann, Engel and Sandor[12] ($\mu = 1.45\ D$).

TABLE II

FLUOROMESITYLENE IN BENZENE

c_2	d	ϵ	P_2	n_D	R_2
0.0000	0.86826	2.2627		1.49448	
.003941	.86881	2.2717	77.4	1.49429	39.9
.007947	.86928	2.2807	77.1	1.49417	40.7
.011819	.86978	2.2885	75.7	1.49396	40.4

CHLOROMESITYLENE IN BENZENE

c_2	d	ϵ	P_2	n_D	R_2
0.0000	0.86841	2.2627		1.49439	
.002953	.86918	2.2725	94.0	1.49443	44.6
.005958	.86987	2.2821	93.5	1.49454	45.7
.009211	.87063	2.2924	93.2	1.49459	45.6
.012176	.87140	2.3014	92.3	1.49471	45.7
.015161	.87209	2.3110	92.4	1.49480	45.8

BROMOMESITYLENE IN BENZENE

c_2	d	ϵ	P_2	n_D	R_2
0.00000	0.86841	2.2627		1.49467	
.002052	.86987	2.2697	96.6	1.49482	48.9
.003980	.87124	2.2764	97.1	1.49501	49.4
.005940	.87264	2.2832	97.1	1.49523	49.5
.007779	.87396	2.2896	97.2	1.49547	49.8
.009963	.87546	2.2975	97.8	1.49556	49.4

IODOMESITYLENE IN BENZENE

c_2	d	ϵ	P_2	n_D	R_2
0.0000	0.86812	2.2627		1.49461	
.002987	.87164	2.2725	96.5		
.006043	.87520	2.2828	97.2	1.49575	55.6
.009001	.87871	2.2933	98.1	1.49632	55.4
.012165	.88240	2.3037	97.7	1.49665	54.4

NITROMESITYLENE IN BENZENE

c_2	d	ϵ	P_2	n_D	R_2
0.0000	0.86827	2.2627			
.001373	.86880	2.2879	319.3	1.49497	
.002974	.86929	2.3181	319.2		
.004369	.86975	2.3439	317.3		
.005860	.87032	2.3713	314.9	1.49521	49.9

NITROMESITYLENE IN CCl_4

c_2	d	ϵ	P_2	n_D	R_2
0.0000	1.5746	2.2157			
.001443	1.5735	2.2395	315.0		
.002971	1.5722	2.2657	319.6		
.004438	1.5710	2.2896	315.6		
.006026	1.5698	2.3222	326.4		

MESITOL IN BENZENE

c_2	d	ϵ	P_2	n_D	R_2
0.0000	0.86811	2.2627		1.49514	
.001916	.86846	2.2680	82.3		
.004875	.86893	2.2762	82.2		
.007868	.86932	2.2846	83.0	1.49567	44.0

FLUOROBENZENE IN BENZENE

c_2	d	ϵ	P_2	n_D	R_2
0.0000	0.86819	2.2629		1.49420	
.003811	.86879	2.2734	69.5	1.49403	25.4
.007683	.86931	2.2839	69.1	1.49386	25.8
.011696	.86990	2.2956	69.7	1.49373	26.1
.015591	.87051	2.3067	69.6	1.49358	25.9

TABLE III

Compound	Solvent	P_2^∞	R_2	$\mu \times 10^{18}$
Fluoromesitylene	C_6H_6	78.0	40.4	1.36
Chloromesitylene	C_6H_6	94.5	45.7	1.55
Bromomesitylene	C_6H_6	96.5	49.4	1.52
Iodomesitylene	C_6H_6	96.5	55.0	1.42
Nitromesitylene	C_6H_6	323	49.9	3.65
Nitromesitylene	CCl_4	319	49.9	3.63
Mesitol	C_6H_6	82.0	44.0	1.36
Fluorobenzene	C_6H_6	69.5	25.8	1.46

The value reported here ($\mu = 1.46\ D$) is in close agreement with that of the latter workers. We wish to thank Miss Gorman for permission to include it here.

Discussion.—We have calculated the dipole moments of the mono-substituted mesitylenes measured here from the moments of the corresponding mono-substituted benzene derivatives using the method of Smallwood and Herzfeld.[13] Calculations for mesitol are not included as these have to take into account the rotation of the hydroxyl group. We expect to carry these out in connection with another series of measurements on compounds with rotating groups.[1a]

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[9] Hammick, New and Williams, *J. Chem. Soc.*, 29 (1934).

[10] One Debye (D) = 1×10^{-18} e. s. u.

[11] Walden and Werner, *Z. physik. Chem.*, **B2**, 10 (1929).

[12] Bergmann, Engel and Sandor, *Z. physik. Chem.*, **B10**, 106 (1930).

[13] Smallwood and Herzfeld, THIS JOURNAL, **52**, 1920 (1930).

The calculations make allowance for the mutual interactions by induction of all of the substituent groups in these mesitylene derivatives. They also take into account the moments induced by these groups in the C–C bonds of the ring as was done by Smallwood and Herzfeld in the more complete treatment given in the latter part of their paper. For further details of the method of calculation and the assumptions underlying it, reference should be made to their paper. Employment of this procedure results in the following equation which gives the calculated dipole moment μ_C of a mono-substituted mesitylene, in terms of the observed moment μ_B of the corresponding benzene derivative. α_S is the polarizability of the substituent group and α_C, α_H and α_{CH_3}, are those of the C–C, C–H and C–CH_3 bonds, respectively. r is the radius of the carbon atom in aromatic compounds and μ_{CH_3} the bond moment of the CH_3 group.

$$\mu_C = \frac{\mu_B}{2.627r^3}(r^3 + 0.5806\alpha_C - 0.00926\alpha_{CH_3} + 0.0178\alpha_H) + \frac{0.1018\mu_{CH_3}(\alpha_S - \alpha_H)}{2.627r^3}$$

On substitution of the proper values this reduces to the equation

$$\mu_C = 0.9766\mu_B + 0.0401\alpha_S - 0.0262$$

For the α terms the values in the table given by Smallwood and Herzfeld were used. For μ_{CH_3} the value 0.37 D was used from the measurements of Smyth and McAlpine[14] on toluene vapor. The value of r we have taken as 0.71 Å., which is one-half of Pauling's[15] value for the carbon–carbon distance in aromatic compounds instead of the value 0.75 Å. used by Smallwood and Herzfeld. The use of this value for r also results in a value of 2.627 for the constant in the above equation instead of the value 2.38 given by Smallwood and Herzfeld in their equation 7. The latter equation is used by them in evaluating the inherent group moments from the observed values of the mono-substituted benzene derivatives.[16]

Table IV gives the calculated value μ_C for the moments together with the values of μ_B for the corresponding benzene derivatives which were employed in the calculations. These values of μ_B are the averages of the most recent values among those listed in Smyth's tabulation.[17] The value of μ_B used for fluorobenzene is that reported here. The polarizabilities α_S are those given by Smallwood and Herzfeld except for the C–F group. This was calculated from the value 0.950 of the atomic refraction at infinite wave length given by Schiemann[18] for fluorine.

TABLE IV

Substituent	μ_B	α_S	μ calc. $\times 10^{18}$	μ obs. $\times 10^{18}$
F	1.46	0.607	1.42	1.36
Cl	1.56	2.51	1.60	1.55
Br	1.50	3.63	1.58	1.52
I	1.27	5.46	1.43	1.42
NO_2	4.00	2.75	3.99	3.64

The agreement is seen to be quite good except in the case of nitromesitylene. Smallwood and Herzfeld found similar deviations in the case of some benzene derivatives where the nitro group was one substituent. It is probable that these deviations are ascribable to our lack of knowledge of the exact location of the largest effective dipole within the nitro group which contributes to its total group moment. It seems unlikely that this is situated at the periphery of the carbon atom to which the nitro group is attached as was here assumed. Because of its large value even a small change in the location of this moment for the nitro group would have a significant effect on the calculated value for the total moment of nitromesitylene.

The agreement in the case of iodomesitylene would seem to afford good evidence of the general correctness of the induced moment calculation. In this case the iodine atom because of its size and its large deformability might be expected to be affected considerably by the close proximity of the two methyl groups in the ortho positions.

Summary

The dipole moments of fluoro, chloro, bromo, iodo and nitro mesitylene and of mesitol and fluorobenzene have been determined in solution in benzene at 30°. The moments of the mesitylene compounds are compared with those calculated from the moments of the corresponding mono-substituted benzene derivatives using the method of Smallwood and Herzfeld.

DURHAM, NORTH CAROLINA RECEIVED MARCH 10, 1934

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[14] Smyth and McAlpine, THIS JOURNAL, **55**, 459 (1933).

[15] Pauling, *Proc. Nat. Acad. Sci.*, **18**, 295 (1932).

[16] Compare Ref. 13, p. 1926.

[17] "Dielectric Constant and Molecular Structure," The Chemical Catalog Co., New York, 1931, Appendices I and II.

[18] Schiemann, *Z. physik. Chem.*, **156A**, 402 (1931).