300°K. The following entropy values at 298.1 were calculated: 79.8 cal./deg. mole for potassium chloroplatinate, 49.7 cal./deg. mole for tetramethylammonium iodide and 120.9 cal./deg. mole for uranyl nitrate hexahydrate.

The heats of solution of each of these three salts has been determined at 25°.

The following partial molal entropy values have been determined: 53.2 cal./deg. mole for $PtCl_6^=$, 50.3 cal./deg. mole for $(CH_3)_4N^+$ and −17 cal./deg. mole for UO_2^{++}. Suggestions have been offered accounting for the apparent deviation of the ionic entropy of UO_2^{++} from an expected value.

The free energies of formation of $PtCl_6^=$ and UO_2^{++} have been obtained.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, DUKE UNIVERSITY]

The Electric Moments of Some Substituted Benzoic Acids

BY CLYDE S. BROOKS AND MARCUS E. HOBBS

Introduction

The direction of the group moment associated with the carboxyl group apparently has never been determined. The present measurements of the electric moments of chlorobenzene, bromobenzene, benzoic acid, *m*- and *p*-chlorobenzoic acid and *m*- and *p*-bromobenzoic acid were carried out because the approximate direction of this group moment was necessary in connection with a systematic study of the acids[1] that is being conducted in this Laboratory. The acids are normally associated even in dilute (10^{-3} mole fraction) solutions of benzene and similar substances. Therefore dioxane was used as the solvent as it apparently will inhibit the acid association because of the formation of a hydrogen bond between the acid monomer and the oxygen of the dioxane. Another interest in connection with these measurements was whether resonance of the carboxyl group with the ring inhibited free rotation about the C–C linkage. The meta compounds were measured with this in mind. A further purpose was to determine whether deviations from additivity were encountered when the resonating halogen and carboxyl group were located para to each other. Deviations of this type have been observed in the case of *p*-nitroaniline and have been explained by Pauling[2] as due to the resonance phenomenon.

Materials and Procedure

Dioxane.—Carbide and Carbon Chemicals Co. dioxane essentially free from peroxides was dried with calcium chloride and then distilled from sodium through a 180-cm. Dufton column. The middle fraction boiling at 101.25–101.45° (cor.) was used.

Chlorobenzene.—Eastman Kodak Co. highest purity chlorobenzene was dried with "Drierite" and then distilled through a 40-cm. Widmer column. The middle fraction boiling at 132.10–132.12° (cor.) was used.

Bromobenzene.—Eastman highest purity product was dried overnight with phosphorus pentoxide and then distilled through a 40-cm. Widmer still. The fraction boiling at 156.17–156.18° (cor.) was used.

Benzoic Acid.—Sublimed benzoic acid was recrystallized from anhydrous benzene; melting point by cooling curve 121.8–121.9°.

***p*-Chlorobenzoic Acid.**—Eastman highest purity product was recrystallized from a one to one mixture of dioxane and benzene. A sharp m. p. at 240° was unchanged by further recrystallization.

***p*-Bromobenzoic Acid.**—Eastman highest purity product was recrystallized from a one to one mixture of dioxane and benzene. The m. p. at 254° was unchanged by further recrystallization.

***m*-Chlorobenzoic Acid.**—Eastman best grade was recrystallized from benzene; melting point by cooling curve 154.8–154.9°.

***m*-Bromobenzoic Acid.**—Eastman best grade was recrystallized from a one to one mixture of dioxane and benzene and then twice from anhydrous benzene. The m. p. of 156° was unchanged by further recrystallization.

The procedure has been described previously.[3] The average density of the dioxane at 30° was 1.0207. Its dielectric constant at 30° was taken as 2.2310.[4]

Calculations and Data

The calculation of the polarization per gram of solute, p_2, was made with the following equation.[1]

$$p_2 = \frac{1}{\epsilon_{12} + 2}\cdot\frac{1}{d_{12}}\left\{\epsilon_{12} - 1 + \frac{W_1}{W_2}[(0.7091)(\Delta\epsilon) - (1.206)(\Delta d) - (0.285)(\Delta\epsilon)(\Delta d)]\right\}$$

In this expression ϵ_{12} is the dielectric constant of

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[1] Pohl, Hobbs and Gross, *Annals of the New York Academy of Science*, Dielectrics, in press (1940).

[2] L. Pauling, "Nature of the Chemical Bond," 1st edition, Cornell University Press, Ithaca, N. Y., 1939, p. 204.

[3] De Bruyne, Davis and Gross, THIS JOURNAL, **55**, 3936 (1933).

[4] Ulich and Nespital, *Z. physik. Chem.*, **B16**, 229 (1932).

the solution, d_{12} the density of the solution, W_1/W_2 the weight ratio of solvent to solute, $\Delta\epsilon$ the difference between the dielectric constant of the solution and that of the solvent, and Δd the difference in density of the solution and solvent. The constant 0.7091, a characteristic for the solvent, is obtained from the expression

$$C_1 = -(p_1 d_1 - 1)$$

Here C_1 is the constant, p_1 is the polarization per gram of solvent, and d_1 is the density of the solvent. The constant 1.206 is obtained from

$$C_2 = p_1(\epsilon_1 + 2)$$

where C_2 is the constant and ϵ_1 is the dielectric constant of the solvent. The constant 0.285 is the value of p_1 for the solvent.

The equation for p_2 is useful in that it allows a rapid slide rule calculation of the polarization with an entirely unapproximated expression of the regular Debye equation. The data in Table I are the mole fraction of solute, f_2, the increment in density, Δd, the increment in dielectric constant, $\Delta\epsilon$, and the molar polarization of the solute, P_2. The value of P_2 listed at the bottom of each set of data is the average value found for that compound and is the value used in the calculation of the electric moment. This procedure of averaging is permissible since the limited solubility of the substituted acids made it impossible to measure solutions of sufficiently high concentration to cause observable dipole–dipole interaction effects. R_D is the molar refraction calculated from the atomic refraction for the Na_D line; μ is the calculated dipole moment expressed in Debye units. No account was taken of the atomic polarization. All measurements were made at 30.0°.

TABLE I

f_2	$\Delta d(10^3)$	$\Delta\epsilon(10^3)$	P_2
	Chlorobenzene		
0.01482	2.0	59.3	86
.01710	2.2	66.6	86
.02510	3.7	93.7	82
.02995	4.2	114.0	83
	$P_2 = 84$; $R_D = 31.1$; $\mu = 1.61$		
	Bromobenzene		
0.00968	6.2	37.7	85
.01438	8.8	57.2	86
.01914	11.2	74.5	86
.02820	16.1	105.8	84
	$P_2 = 85$; $R_D = 34.0$; $\mu = 1.58$		
	Benzoic Acid		
0.01100	2.9	49.8	96
.01486	3.3	70.9	98
.01894	4.4	93.8	98
.03185	6.9	148.0	95
	$P_2 = 97$; $R_D = 32.4$; $\mu = 1.78$		
	p-Chlorobenzoic Acid		
0.01006	4.9	60.6	118
.01364	6.3	82.1	119
.01885	8.3	109.6	116
.02238	12.2	147.0	123
	$P_2 = 119$; $R_D = 37.3$; $\mu = 2.00$		
	p-Bromobenzoic Acid		
0.00419	5.3	28.6	131
.00845	8.9	56.9	128
.01327	13.0	84.7	124
.01413	13.1	91.0	127
	$P_2 = 128$; $R_D = 40.2$; $\mu = 2.08$		
	m-Chlorobenzoic Acid		
0.00993	5.5	73.2	136
.01438	6.8	107.0	138
.01742	8.3	120.6	131
.01825	8.6	134.4	137
	$P_2 = 136$; $R_D = 37.3$; $\mu = 2.20$		
	m-Bromobenzoic Acid		
0.00436	4.4	30.0	131
.01068	11.1	75.9	133
.01580	15.7	119.3	139
.02010	18.6	139.5	132
	$P_2 = 134$; $R_D = 40.2$; $\mu = 2.15$		

Discussion

Wilson and Wenzke[5] have shown that the values of the dipole moment for acetic and propionic acids obtained from measurements in dilute solutions of dioxane are in good agreement with the values for the single molecules in the gas state.[6] This probably indicates that the effects of solvent–solute interactions on the moment are not so serious as to invalidate the results obtained. Therefore it is felt that the values for the acids given in Table I probably represent the proper dipole moment of the molecule for the purpose to which it will be put in the present discussion. The possibility of a cancellation of some moments due to a double hydrogen bond on any one dioxane molecule is rather small in the dilutions used; furthermore, there is apparently no regular trend in the polarization as a function of concentration such as one would expect if any sensible quantity of such association occurred.

In Table II are listed the values of the moments obtained.

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(5) Wilson and Wenzke, *J. Chem. Phys.*, **2**, 546 (1934).

(6) C. T. Zahn, *Phys. Rev.*, **37**, 1516 (1931).

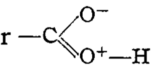
TABLE II

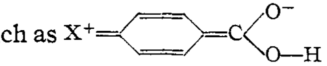
Substance	μ
Chlorobenzene	1.61
Bromobenzene	1.58
Benzoic acid	1.78
p-Chlorobenzoic acid	2.00
p-Bromobenzoic acid	2.08
m-Chlorobenzoic acid	2.20
m-Bromobenzoic acid	2.15

A previous measurement of chlorobenzene in dioxane by Williams[7] indicated a moment of 1.54 *D*. In benzene the best value is probably 1.56 *D*. Apparently bromobenzene has not been measured in dioxane, but its value in benzene is 1.53 *D*. Benzoic acid had been measured[8] in dioxane and the value 1.71 *D* obtained. In the calculation of this moment the electron polarization term was taken as 34.1 cc. If it is taken as 32.4 cc., as in our case, the calculated moment becomes 1.74 *D*. The other substances listed have not been measured before.

The approximate angle that the carboxyl group moment makes with the C–C line may be determined by solving for θ in the following equation in which the resultant is that of the para compounds.

$$\mu^2 = \mu_1^2 + \mu_2^2 - 2\mu_1\mu_2 \cos\theta$$

Here μ_1 is the component moment 1, μ_2 the component moment 2, and θ the supplement of the angle between the two vectors μ_1 and μ_2. For *p*-chlorobenzoic acid one obtains $\theta = 72°$ and for *p*-bromobenzoic acid $\theta = 76°$. Neither of these figures is regarded as particularly accurate but for reasons mentioned later it is felt that the value of $\theta = 76°$ is probably the best value. This may be compared with the value calculated on the basis of additivity of bond moments in the carboxyl group. If values of 2.4, 1.5, and 0.9 are taken for the C═O, O—H, and C—O bond moments, respectively, and the C—O to O—H angle is taken as 110° and the C═O to C—O taken as 125°, the calculated angle is 85° and the resultant is 1.1 Debye units. This discrepancy both as to angle and moment is rather large. Its explanation probably lies in the fact that contributions from the resonance structure for  $-\mathrm{C}(\mathrm{O}^-)\mathrm{O}^+\mathrm{—H}$ were not properly considered in the above calculations. As Pauling[9] has pointed out, the resonance energy is quite large; thus it would seem that this structure might contribute considerably to the total structure. If, as an approximation, one considers that the normal covalent radii[10] are valid in the carboxyl group, then the contribution to the resolved dipole moment of 1.1 from the resonance structure is in the correct direction to increase the total moment and in fact is parallel to the resultant obtained without considering this contribution. The shortening of the C–O bond and a lengthening of the C═O bond due to resonance would cause the total carboxyl resultant to more nearly approximate the observed resultant both as to magnitude and direction.

The values listed in Table II show that *p*-chlorobenzoic acid has a lower moment than *p*-bromobenzoic acid. This is somewhat the reverse of what might be expected on the basis of their component moments and the discrepancy is probably due to a resonance effect. If structures such as  make contributions to the moments of the para compounds, it is likely that the discrepancy may be due to the greater ease[11] with which chlorine resonates as compared to bromine. The cases[12] of *p*-chloronitrobenzene and *p*-bromonitrobenzene show differences in which the deviation of observed from calculated are positive and are in such direction that the deviation for the bromo compound exceeds that for the chloro compound. In these last two cases the dipole vectors are anti-parallel. In *p*-nitroaniline the deviation of observed from calculated is quite positive. In this case the dipole vectors are parallel. As mentioned previously, the *p*-nitroaniline discrepancy has been attributed to resonance and undoubtedly the discrepancies in the *p*-chloro and *p*-bromonitrobenzenes may be explained on the same basis. In the case of the acids the deviations from additivity are, of course, not calculable simultaneously with the angle, but the difference between the chloro and bromo compounds, although small, is probably an evidence of the same phenomenon as that present in the cases cited.

In connection with the problem of free rotation of the carboxyl group the meta compounds measured cannot answer the question definitively. The value predicted for meta substituted acids on the basis of free rotation may be obtained from

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[7] J. W. Williams, THIS JOURNAL, **52**, 1831 (1930).

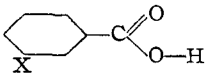
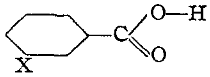
[8] Wilson and Wenzke, *ibid.*, **57**, 1265 (1935).

[9] Ref. 2, p. 130.

[10] Ref. 2, p. 154.

[11] Ref. 2, p. 216.

[12] L. Tiganik, *Z. physik. Chem.*, **B13**, 425 (1931).

the expression $\mu^2 = \mu_x^2 + \mu^2_{y_1} + \mu^2_{y_2}$, where μ_x is the resultant of the x component of the group moments 1 and 2, and μ_{y_1} and μ_{y_2} are the y components of group moments 1 and 2, respectively. The values obtained are 2.23 for the chloro compound and 2.21 for the bromo compound. These are in reasonably good agreement with the observed values, since the discrepancies are of the same order as those observed in other meta compounds (*i. e.*, *m*-dichlorobenzene calcd. 1.55, obsd. 1.48). The meaning of this agreement is not clear since the same values are obtained if one considers an equal mixture of the two molecules represented by  and  The assumption is that in these molecules the carboxyl group is coplanar with the ring.

Another line of attack on the free rotation question is to measure compounds in which the rotation would be definitely prevented and in which the resonance structure would be inhibited. This condition has been realized in nitrodurene[13] and in the nitromesitylenes.[14] A very considerable reduction of the moment is observed if the values for these compounds are compared to that of nitrobenzene. The contribution to the moment of nitrobenzene from resonance structure is, however, quite large (*ca.* 0.6 Debye unit) compared to that which is apparently obtained in the case of the acids. In fact, so far as can be judged, the moment contribution due to resonance structures involving the ring and carboxyl group must be rather small as the aliphatic and aromatic acids have essentially the same moment. It may be mentioned that an evaluation of Ri and Eyring[15] shows the resonance charge in the ring for benzoic acid and nitrobenzene to be nearly the same; however, one must notice that the value of 1.0 calculated for the dipole moment of benzoic acid is probably wrong. The value 1.0 is to be associated[1] with the dimer of the acid.

Summary

The electric moments of chlorobenzene, bromobenzene, benzoic acid, *m*- and *p*-chlorobenzoic acid and *m*- and *p*-bromobenzoic acid have been measured using dioxane as the solvent. The moments found are used in an evaluation of the direction of the carboxyl group moment and in an attempt to determine whether or not the carboxyl group is in free rotation. The mean direction of the moment was found to be 74° with respect to the C–C line. No conclusion as to free rotation could be drawn as the results would not allow one to distinguish between free rotation and an equimolar mixture of molecules in which the carboxyl group is fixed in the plane of the ring with the O–H in a *cis* and *trans* position with respect to the meta substituent. A small discrepancy between the expected and observed values of *p*-chlorobenzoic acid and *p*-bromobenzoic acid is attributed to a resonance effect between the halogen and carboxyl groups substituted on the benzene ring.

Durham, N. C. Received July 17, 1940

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[13] Ref. 2, p. 205.

[14] Jacokes, Brown and Gross, unpublished results in this Laboratory.

[15] Ri and Eyring, *J. Chem. Phys.*, **8**, 433 (1940).