TABLE I

REDUCTION OF ACETYLENES AT A SPONGY NICKEL CATHODE IN ALCOHOLIC SULFURIC ACID

Acetylene	Product	Yield, %	B. p., °C.	Press., mm.	$n^{20}D$	d^{20}_4	F. p., °C.
5-Decyne	*cis*-5-Decene	75	73°	30	1.4253	0.7445	−111
			73[a]	30	1.4252	.7445	−112
4-Octyne	*cis*-4-Octene	80	72	150	1.4139	.7212	−116
			73[b]	150	1.4136	.7205	−118
1-Heptyne	1-Heptene	65	93	740	1.3978	.6945	
Phenyl	Ethylbenzene and styrene	..	76–78	80	1.5007–1.5461		
Diphenyl	*cis*-Stilbene	80	145	18	1.6265		

[a] Results obtained by Campbell and Eby[6] for *cis*-5-decene. [b] Results obtained by Campbell and Eby[7] for *cis*-4-octene.

olefins. The results are summarized in Table I. Reduction of phenylacetylene at a spongy nickel cathode yielded a liquid, b. p. 76–78° (80 mm.), $n^{20}D$ 1.5007–1.5461, which appeared to be a mixture of ethylbenzene and styrene. It gave no precipitate with ammoniacal cuprous chloride. Styrene dibromide, m. p. 72–73°, was obtained by bromination of the portion with the highest index of refraction. The reduction product from tolane was shown to be *cis*-stilbene, for when it was treated with a very small amount of benzoyl peroxide and hydrogen bromide, and exposed in a quartz test-tube to the rays of a quartz mercury vapor lamp for thirty minutes it was converted to *trans*-stilbene, m. p. 123–124°.[11]

Reduction at Other Cathodes.—Attempts to reduce 5-decyne at a copper cathode plated with spongy copper yielded largely unchanged 5-decyne, but about 0.5 g. of material was obtained of b. p. 74° (30 mm.), $n^{20}D$ 1.4260; this appeared to be *cis*-5-decene. No reduction of 5-decyne could be obtained at a spongy cadmium cathode, in acid or alkaline solution, nor at a lead cathode in alkaline solution. Attempts to reduce 5-decyne and tolane at an amalgamated mercury cathode in acid and alkaline solution were unsuccessful. No reduction of 5-decyne was obtained when a platinum cathode was used, even in the presence of "carriers" such as chromic sulfate.

Summary

It has been shown that alkyl and aryl acetylenes can be reduced at a spongy nickel cathode in acid solution. 5-Decyne, 4-octyne and diphenylacetylene yield the *cis*-olefins, phenylacetylene gives a mixture of ethylbenzene and styrene and 1-heptyne yields 1-heptene. No reduction occurs at cathodes of cadmium, lead, amalgamated lead or platinum; very little reduction occurs at a copper cathode.

NOTRE DAME, INDIANA RECEIVED FEBRUARY 5, 1943

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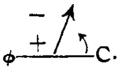
[11] Taylor and Crawford, *J. Chem. Soc.*, 2078 (1938).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF DUKE UNIVERSITY]

The Electric Moments of Some Substituted Benzoic Acids. II. The Moments of *o*-, *m*- and *p*-Fluorobenzoic Acids, and of *o*-Chloro and *o*-Bromobenzoic Acids

BY MARCUS E. HOBBS AND ARCHIE J. WEITH, JR.

Introduction

In the first paper[1] of this series the electric moments of the *meta*- and *para*-chloro and bromobenzoic acids were reported. It was pointed out there that apparently the resultant of the carboxyl group moment makes an angle of 72–76° with respect to the phenyl-carbon axis, *viz.*, 

. The present measurements of the three fluorobenzoic acids and of *o*-chloro and *o*-bromobenzoic acids were made in order to complete the chloro and bromo series, and to use the new fluoro series better to establish the value of the angle mentioned above. The fluoro acids were also of special interest to us since monomer-dimer equilibrium studies[2] by the dielectric polarization method had been carried out on these acids in this Laboratory. In the course of the above study the values of the electric moments of the unassociated acid molecules in benzene solution were calculated. We wished to compare the values thus obtained with those observed in dioxane solution where the acid molecule is hydrogen bonded to the solvent molecule.

Experimental

Dioxane.—Carbide and Carbon Chemicals Corp. dioxane, free from peroxides, was dried and refluxed with solid potassium hydroxide until discoloration practically ceased.

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[1] Brooks and Hobbs, THIS JOURNAL, **62**, 2851 (1940).

[2] Maryott, Hobbs and Gross, *J. Chem. Phys.*, **9**, 415 (1941).

It was then refluxed for twelve hours over sodium and then distilled from sodium through a 180-cm. Dufton column. The fraction boiling at 101.16–101.20° (cor.) was used as the solvent for the measurements.

Fluorobenzene.—Eastman Kodak Co. best grade was dried over calcium chloride and then fractionally distilled through a 40-cm Widmer column. The fraction boiling at 84.68° (cor.) was used in the measurements.

***o*-Chlorobenzoic Acid.**—Eastman Kodak Co. highest purity product was recrystallized two times from dioxane–benzene solution. The sample used had a m. p., by the capillary tube method, of 139.8–140.0°.

***o*-Bromobenzoic Acid.**—Eastman Kodak Co. best grade was recrystallized twice from dioxane–benzene solution. The sample used had a m. p. of 148.5–148.7°.

***o*-Fluorobenzoic Acid.**—This was prepared from carefully purified Eastman Kodak Co. best grade *o*-fluorotoluene by the oxidation procedure[3] for preparing *o*-chlorobenzoic acid from *o*-chlorotoluene. It was recrystallized three times from benzene, m. p. 123.4–123.6°.

***m*-Fluorobenzoic Acid.**—This was prepared from carefully purified *m*-fluorotoluene by oxidation.[3] The sample used had a m. p., after three recrystallizations, of 122.5–122.8°.

***p*-Fluorobenzoic Acid.**—This was prepared from purified *p*-fluorotoluene by oxidation.[3] After three recrystallizations the product had a m. p. of 180.5–180.7°.

The range in the m. p. given above is taken as the criterion of their purity rather than the actual value of the m. p.

The procedure and apparatus used in making a measurement have been described previously.[4] The average density of the dioxane used was 1.022. Its dielectric constant at 30° was taken as 2.2310.[5]

Calculations and Data

Calculation of the polarization per gram of solute was made using the following expanded form of the Clausius–Mosotti equation

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

This relation has been explained in detail in a previous[1] paper. Briefly, the terms involved have the following meaning. Subscript 1 refers to solvent, and 2 to solute and 12 to solution. ϵ is the dielectric constant, $\Delta\epsilon$ the increment in the dielectric constant of the solution over that of the solvent. Δd is the increment in the density, and W represents weight in grams.

In Table I we have listed the mole fraction of solute f_2, Δd, $\Delta\epsilon$, and the molar polarization of the solute P_2. At the bottom of each series of data we have R_D which is the molar refraction as calculated from the atomic refractions for the Na_D line, $P_{2(av.)}$ which is the average value of P_2 and which is the value used in calculating μ, the electric moment. It is obvious from the data that extrapolation procedure for obtaining a value of P_2 at $f_2 = 0$ is unnecessary. The moment is expressed in Debye units throughout this paper.

Only the densities of the solvent and of the most concentrated solutions were determined. The Δd values for the intermediate concentrations were interpolated on the assumption that $\Delta d/f_2$ was constant. This assumption was checked in the case of *o*-fluorobenzoic acid by measuring Δd at three different concentrations. The value of $\Delta d/f_2$ was constant within 1% for all concentrations that we used. This precision is entirely

TABLE I

$f_2(10^3)$	$\Delta d(10^3)$	$\Delta\epsilon(10^3)$	P_2 (cc.)
	Fluorobenzene		
9.75	−0.05	30.6	73
16.18	− .08	47.0	69
19.39	− .11	59.8	72
28.99	− .16	91.9	73
R_D = 26.1.	$P_{2(av.)}$ = 72.	$\Delta d/f_2$ = −0.005.	μ = 1.50.
	o-Fluorobenzoic Acid		
9.19	3.4	58.4	121
13.17	4.7	78.5	121
15.74	5.8	100.2	122
17.23	6.4	112.3	124
R_D = 32.4.	$P_{2(av.)}$ = 122.	$\Delta d/f_2$ = 0.370.	μ = 2.10.
	m-Fluorobenzoic Acid		
9.64	3.3	65.1	128
12.58	4.3	83.0	127
13.23	4.5	88.3	127
19.44	6.6	129.0	126
R_D = 32.4.	$P_{2(av.)}$ = 127.	$\Delta d/f_2$ = 0.339.	μ = 2.16
	p-Fluorobenzoic Acid		
9.48	3.3	53.2	112
13.49	4.7	75.7	112
15.97	5.5	93.4	115
19.69	6.7	111.4	113
R_D = 32.4.	$P_{2(av.)}$ = 113.	$\Delta d/f_2$ = 0.343.	μ = 1.99.
	o-Chlorobenzoic Acid		
9.69	4.4	84.5	158
14.51	5.6	127.2	158
15.36	7.0	135.3	158
20.00	9.1	179.1	156
R_D = 37.3	$P_{2(av.)}$ = 157.	$\Delta d/f_2$ = 0.454.	μ = 2.43.
	o-Bromobenzoic Acid		
10.01	9.1	91.0	167
10.53	9.3	92.3	167
17.04	15.5	152.9	165
20.08	18.3	184.4	167
R_D = 40.2.	$P_{2(av.)}$ = 167.	$\Delta d/f_2$ = 0.910.	μ = 2.50.

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(3) "Organic Syntheses," **10**, 20 (1930).

(4) de Bruyne, Davis and Gross, THIS JOURNAL, **55**, 396 (1933); Maryott, Hobbs and Gross, *ibid.*, **62**, 2320 (1940).

(5) Ulich and Nespital, *Z. physik. Chem.*, **B16**, 221 (1932).

satisfactory for the Δd values observed in our work and in the light of the precision of the over-all measurement. All measurements were made at 30.0°.

Discussion

The value of $\mu = 1.50$ obtained for fluorobenzene is to be compared with 1.45 reported by Bergmann[6] and Nukada[7] and of 1.46 reported by Brown, de Bruyne and Gross.[8] All of the latter moments were determined by measurement in benzene solution, and our slightly higher value obtained in dioxane solution is in line with similar differences observed with several other compounds that have been measured in these two solvents. The moment of this molecule has been determined in the gas phase by Smyth[9] and Moore,[10] both of whom report 1.57.

As mentioned previously,[2] *o*-, *m*- and *p*-fluorobenzoic acids have been measured in benzene solution, in which they are largely in the associated (dimeric) form. The values for the single molecules reported in the above work are considered to have a precision of about ±0.10–0.15 Debye units. The moments reported were 2.5, 2.2 and 1.9 for the *o*, *m* and *p* cases, respectively. These are to be compared with our values of 2.10, 2.16 and 1.99 for the same sequence. The agreement for the *m* and *p* cases is considered quite satisfactory, but the *o* cases differ by considerably more than can be accounted for by random experimental error. It may be noted that, because of the rather large dissociation of the *o*-acid, its single molecule moment of 2.5 should be better established than either that of the *m* or *p*-acids. A suggestion as to the basis of the ortho case discrepancy is the possibility of internal hydrogen bonding between the H of the carboxyl group and the ortho located fluorine atom when the molecule is in benzene solution, whereas the preferred hydrogen bonding may take place between the solvent and H of the carboxyl in the case of dioxane solutions. This would account for the discrepancy in a qualitative fashion if the internal hydrogen bonded form of the molecule had a higher net moment than that with an external hydrogen bond. Some further discussion of this problem will be given later in this section.

There are apparently no values reported in the literature for *o*-chlorobenzoic and *o*-bromobenzoic acids.

Using the moment of *p*-fluorobenzoic acid, we have calculated that the angle the carboxyl group moment makes with the ϕ–C axis is 74°. This, along with the previously calculated values[1] of 72 and 76° for *p*-chloro and *p*-bromo acids gives an average value for the angle of 74°.

By using this value of the angle and assuming vector additivity of the moments involved we have calculated the values one might obtain for the various substituted acid molecules measured. These values are listed along with the observed values in Table II. Δ in this table is the difference between the calculated and observed values. In making the calculations the assumption has been made that there is an equal mixture of "*cis*" and "*trans*" forms[1] of the molecule concerned. This is equivalent, so far as dipole calculations are concerned, to free rotation about the ϕ–C bond.

TABLE II

	$\mu_{\text{obs.}}$	$\mu_{\text{calcd.}}$	Δ
Benzoic acid[11]	1.78		
Fluorobenzene	1.50		
o-Fluorobenzoic acid	2.10	2.48	0.38
m-Fluorobenzoic acid	2.16	2.15	− .01
p-Fluorobenzoic acid	1.99	1.99	.00
Chlorobenzene[11]	1.61		
o-Chlorobenzoic acid	2.43	2.56	.13
m-Chlorobenzoic acid[11]	2.20	2.24	.04
p-Chlorobenzoic acid[11]	2.00	2.04	.04
Bromobenzene[11]	1.58		
o-Bromobenzoic acid	2.50	2.54	.04
m-Bromobenzoic acid[11]	2.15	2.21	.06
p-Bromobenzoic acid[11]	2.08	2.03	− .05

Included in Table II are the calculated values for the para compounds; however, since they were used in establishing the average value of the angle for the carboxyl group moment their calculated value is not independent of the observed value. The average value of 74° was used in calculating the para cases as well as all of the others.

On examination of the deviations, Δ, in Table II we see the only ones of significance are for *o*-chlorobenzoic and *o*-fluorobenzoic acids. Too much weight must not be attached to agreement, or lack of it, between the calculated and observed values; however, it seems proper that we might consider at this point some of the factors which may cause the above deviations. (1) The possibility of resonance structures contributing to

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(6) Bergmann, Engel and Sandor, *Z. physik. Chem.*, **B10**, 106 (1930).

(7) Nukada, *Nia Kemio.*, **5**, 41 (1932).

(8) Brown, de Bruyne and Gross, THIS JOURNAL, **56**, 1291 (1934).

(9) MacAlpine and Smyth, *J. Chem. Phys.*, **3**, 55 (1935).

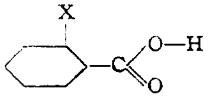
(10) E. M. Moore, unpublished data from this Laboratory.

(11) Ref. 1, p. 2853.

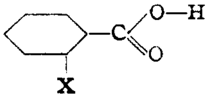
electric moments has been suggested quite often and in many cases these effects have a first order influence in determining the value of the moment. In general the first order effects are found within a particular polar group, but occasionally groups with great tendencies to form "resonance structures" will interact with each other and produce effects that may be regarded as first order deviations. Such a case as the moment of *p*-nitroaniline may be cited. Furthermore, it might well be expected that unless the interaction between the groups could take place through an ordinary (as distinguished from a hyperconjugated) conjugated system its contribution to the total deviation effects would be small. (2) Another effect that has been considered as a source of dipole moment deviations is the inductive effects such as those exhibited so markedly in the substituted benzene ring. In general one might expect these effects to be rather small except at rather close distances or in cases where the bond electron densities are such as to allow the effect to be transmitted rather freely along the bonds. The latter cases are of course the conjugated systems. Ri and Eyring[12] have calculated the inductive effects in the substituted benzene ring and find that, in general, the inductive effect exceeds, or equals, the resonance effects. The one significant exception in their calculations is the case of toluene. It is felt by the present authors that many of the deviations that have been observed in electric moment investigations are due to the inductive effects transmitted along the bond lines rather than to dipole polarizability interaction effects. A recent paper by Remick[13] gives some quantitative calculations of this effect, and in another paper[14] by one of the present authors an attempt was made to explain deviation effects by this means. Smyth[15] has recently suggested that contributions from hyperconjugated structures might offer a more specific mechanism to explain deviations considered in references 14 and 15. (3) Still another effect that has been used frequently to explain deviations is the previously referred to direct dipole-polarizability interactions which take place through the intervening space between the groups concerned. This effect is a rather short range one and except for effects between ortho substituted groups or groups separated by equivalent distances the deviations are likely to be small. (4) The last factor that we will consider that might give rise to deviations from additivity is the possibility that, due to the mutual influence of the substituents, a change in the normal structure of either or both of the groups concerned might occur. Further, it is possible that due to mutual interaction of the substituent groups some one form of an isomeric mixture will be favored, and as a consequence the relative proportion of this form would be increased. If the electric moment for the favored isomer is different from the moment of the other forms of the normal mixture, a deviation would, in general, be expected.

On examining the data in Table II in the light of the above discussion we find the most significant deviation is for the case of the least polarizable atom. This leads one to believe that dipole interaction is not the reason for the deviation unless it is of such character as to compensate for the deviations that occur in the case of the chloro and bromo acids. Fluorine is slightly more capable of resonance than chlorine and chlorine somewhat more than bromine. In the light of this and the order of the deviations in the table it seems possible that resonance structure contributions might account for some of the deviations observed. The inductive effect for fluorine is somewhat less than that for chlorine and bromine according to Ri and Eyring.[12] In view of this one might expect a greater decrease in the effective value of the fluorine moment than that of the chloro and bromo compounds because the ring electron charge has been reduced by the carboxyl group. We would expect this effect to be most noticeable in the ortho case.

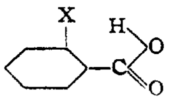
In considering the possibility that there may be a favored form of the acid caused either by the ring substituent, or by solvent interaction, one may write the following as probable isomeric components of the ortho acids.



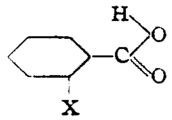
I *cis*



I *trans*



II *cis*



II *trans*

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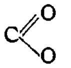
(12) Ri and Eyring, *J. Chem. Phys.*, **8**, 433 (1940).

(13) A. E. Remick, *ibid.*, **9**, 653 (1941).

(14) Maryott, Hobbs and Gross, THIS JOURNAL, **63**, 659 (1941).

(15) Hurdis and Smyth, *ibid.*, **64**, 2829 (1942).

We have evaluated the relative values of the moments of the above forms by means of addition of the bond moment vectors and find that they have moments in the ratio of 1, 2.6, 3.7 and 4.8 for I *cis*, I *trans*, II *cis* and II *trans*, respectively. The carboxyl group has been considered as coplanar with the benzene ring in all calculations. The H atom tends to stay locked in the same plane as the  $\mathrm{C}\begin{matrix}\diagup\!\!\diagup\mathrm{O}\\ \diagdown\mathrm{O}\end{matrix}$ group because of the resonance in this group and, further, tends to stay in form I configuration because of the relatively large interaction energy between the O–H dipole and the C=O dipole. Form II of the above structures is not regarded as particularly probable except for the case of a highly electro-negative group at the ortho position which does not sterically hinder this configuration of the O–H group. It may be remarked that the small resonance energy between the carboxyl and phenyl group would probably not restrict the structures considered to only the coplanar ones; however, since our discussion is entirely qualitative, we have neglected other than planar configurations.

If fluorine is the X atom of the above structures, we might expect real contributions from form II *cis*. It is to be noted, however, that the presence of a hydrogen bonding solvent such as dioxane would probably prevent the existence of much of this form. As pointed out earlier, in the case of benzene solutions the situation might be entirely different.

In general then, we may conclude this section by stating that resonance, inductive and dipole interaction effects all probably contribute to the deviations we have observed and listed in Table II. It must be emphasized, however, that mere agreement between calculated values and observed values is very insufficient basis for attributing all effects to any one cause. It is equally hazardous to accept the agreement as evidence that no factors causing deviations are active.

Summary

The electric moments of *o*, *m* and *p*-fluorobenzoic acids and of *o*-chloro- and *o*-bromobenzoic acids have been determined in dioxane solutions. The values found were 2.10, 2.16, 1.99, 2.43 and 2.50, respectively. Calculation of the angle the carboxyl group moment makes with the ϕ–C axis gives a value of 74° if the moment of *p*-fluorobenzoic acid is used. This along with previously determined angle values from *p*-chloro- and *p*-bromobenzoic acid gives an average value of 74°. A discussion is given of factors which might contribute to deviations between observed values of moments and those calculated by vector addition of the component moments.

DURHAM, N. C. RECEIVED FEBRUARY 20, 1943

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF RUTGERS UNIVERSITY]

The Solubility Product of Barium Chromate at Various Ionic Strengths

BY GEORGE L. BEYER AND WILLIAM RIEMAN III

The values previously reported for the solubility of barium chromate in water vary greatly. Schweitzer[1] in 1890 reported that at room temperature the ordinary salt had a solubility of 4 × 10^{-5} mole per liter of solution, while the ignited salt gave a solubility of 2.5 × 10^{-5} mole per liter. In 1908 Kohlrausch[2] reported that at 25° the solubility was 1.62 × 10^{-5} mole per liter, and in 1918 Waddell[3] reported a value of 3.1 × 10^{-5} mole per liter. In view of the importance of this precipitate in analytical chemistry, it is desirable to have accurate data regarding its solubility product.

Preparation of Reagents

Barium Chromate.—Solutions of recrystallized reagent-grade barium chloride and sodium chromate were prepared and used to precipitate barium chromate in the presence of an excess of barium chloride (Sample A) and in the presence of an excess of sodium chromate (Sample B). Sample A: Fifty millimoles of sodium chromate in 400 ml. of water was added in about thirty minutes to a mechanically stirred solution containing 60 millimoles of barium chloride in 1600 ml. of water. The mixture was then heated to 95–100° and digested for twenty-four hours at this temperature. After settling, the precipitate was washed in the beaker several times by decantation and was then washed in centrifuge tubes until the washings gave a negative chloride test. The preparation was mixed with water and stored in a Pyrex bottle. Sample B was prepared as follows. Fifty millimoles of barium chloride

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(1) Schweitzer, *Z. anal. Chem.*, **29**, 414 (1890).

(2) Kohlrausch, *Z. physik. Chem.*, **64**, 158 (1908).

(3) Waddell, *Analyst*, **43**, 288 (1918).