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Relative Strengths of Forty Aromatic Carboxylic Acids in Benzene at 25° C.[1]

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The relative strengths of benzoic acid, 31 of its monosubstituted derivatives, 7 disubstituted derivatives, and one trisubstituted derivative have been measured in terms of the equilibrium constants (K'') for association with the reference base 1,3-diphenylguanidine in benzene at 25° C. The measurements were performed spectrophotometrically, using the indicator acid bromophthalein magenta E (tetrabromophenolphthalein ethyl ester) as the reference acid, the equilibrium constant K' for association of the indicator with diphenylguanidine being known from previous work. Equilibrium constants for *p*-orsellinic (2,6-dihydroxy-*p*-toluic) acid and 2,4,6-trinitrobenzoic acid could not be measured, as these acids appear to associate completely with diphenylguanidine under the conditions of the experiments.

Plotting log K'' values against the corresponding pK values for aqueous solutions of the acids gives an essentially linear relationship in the case of acids with *meta*- and *para*-substituents only, but the line for *para*-substituted acids has a slightly different slope from the line for *m*-substituted acids. Similar comparisons were made with published data on relative strengths in alcohols or dioxane-water mixtures. *ortho*-Substituted acids show marked solvent effects. Explanations of the solvent effects have been suggested, and various theoretical implications and possible applications of the results are discussed. The theoretical discussion includes evaluation of constants of the Hammett equation.

1. Introduction

Earlier reports from the Bureau [1][2] have dealt with qualitative and quantitative aspects of acid-base reactions in benzene at 25° C, placing particular emphasis on the behavior of different types of organic bases with the three indicator acids, bromophthalein magenta E (tetrabromophenolphthalein ethyl ester), picric acid, and trinitro-*m*-cresol. In this study information previously gained has been applied in measuring systematically the relative strengths of a group of related carboxylic acids—benzoic acid and various substituted benzoic acids—in benzene. The method consists of determining spectrophotometrically the equilibrium constant for the association of the carboxylic acid with the reference base, diphenylguanidine, in the presence of the indicator acid, bromophthalein magenta E, which competes for the base. Each acid is assumed to react with the base in conformance with the equation

$$\text{B (base)} + \text{A (acid)} \rightleftarrows \text{BA(salt)}.^{3} \qquad (1)$$

The equilibrium involving bromophthalein magenta E (yellow in benzene solution), diphenylguanidine (colorless), and the salt formed by their association (magenta) was previously studied [1 (a), (e)]. The data from this former study, together with absorbance data at 540 mμ obtained in the present study have been used to calculate the equilibrium constants K'' for the association of the various carboxylic acids with diphenylguanidine.

The acids studied included 31 acids having a single substituent atom or group in the *ortho*-, *meta*-, or *para*-position. In addition, 7 disubstituted benzoic acids and 3 trisubstituted acids were studied. Two of these acids—2,6-dihydroxy-4-methylbenzoic (*p*-orsellinic) and 2,4,6-trinitrobenzoic—combined so nearly completely with diphenylguanidine that their association constants could not be measured, and one of the acids (*o*-methoxybenzoic) was so unreactive that its K'' could be only approximately measured.

Benzoic acids have been investigated more extensively than any other group of acids with respect to their comparative strengths in aqueous and nonaqueous solvents (notably alcohols and dioxane-water mixtures). In the discussion to follow, the results of such previous studies are compared with the relative strengths in benzene found in this investigation.

2. Materials

2.1. Miscellaneous

The *benzene* used as solvent was of reagent grade, stated to meet ACS specifications. It was stored for at least a week over anhydrous calcium sulfate, then

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[2] Figures in brackets indicate the literature references at the end of this paper.

[3] The salt BA is considered to consist of hydrogen-bonded ion-pairs. See [1 (g)] and references cited therein.

distilled. A final boiling to remove moisture was performed shortly before use. *Bromophthalein magenta E* (*tetrabromophenolphthalein ethyl ester*) was a part of the product previously described [1 (a)]. A high grade 1,3-*diphenyl-guanidine*, $C_6H_5NH{\cdot}C({=}NH){\cdot}NHC_6H_5$, that had been crystallized from toluene was heated to about 67° in a vacuum oven to remove residual solvent. The melting point of the dried product was 149.4° to 149.9° C, and the purity as indicated by titrations in acetic acid and in aqueous ethanol was 99.8 percent.[4]

2.2. Acids

Table 1 gives the list of acids used, with their melting points. The melting points agreed closely with accepted values in the literature.[5]

a. Acids of Commercial Origin

o-Acetoxybenzoic acid (*acetylsalicylic acid, "Aspirin"*) in tablet form was recrystallized twice from benzene. Insoluble matter was removed in the first recrystallization. After a final washing with cyclohexane the crystals were heated to about 60° in a

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[4] Later experiments have shown that diphenylguanidine can be heated in an ordinary oven for as long as 24 hr at 80° C and for as long as 5 hr at 117° C without any noticeable effect on the melting point or the absorption spectrum in absolute ethanol.

[5] For example, see [2] and other references cited as sources of the *pK* values that are also listed in table 1. In regard to the measurements of the melting point see footnote *b* of table 1. The log *K''* values listed in table 1 are discussed in section 4.

TABLE 1. *List of aromatic carboxylic acids and pertinent physical constants*

Name of acid [a]	Melting point [b]	Purity [c]	Log *K''* in benzene at 25° C [d]	*pK* in water at 25° C [e]
	° *C*	%		
Benzoic	121.8 to 122.5	100.0	5.26	4.20 [f]; 4.21 [g]
Monosubstituted benzoic acids				
o-Acetoxybenzoic (Acetylsalicylic, "Aspirin").	133.5 to 135		5.72	3.48 [h, i]
o-Aminobenzoic (Anthranilic).	146 to 147		4.94	4.95 [j]
m-Aminobenzoic	177 to 178		4.93	4.75 [j]
p-Aminobenzoic	186 to 186.5 d		4.45	4.89 [j]
*o-Bromobenzoic	149 to 149.5		6.17	2.85 [f]
*m-Bromobenzoic	154.5 to 155.5		6.06	3.81 [f, g]
*p-Bromobenzoic	253.5 to 254.5		5.86	3.97 [f]; 4.00 [g]
*o-Chlorobenzoic	141 to 142		6.08	2.94 [f]
*m-Chlorobenzoic	155 to 156		6.06	3.83 [f, g]
*p-Chlorobenzoic	239 to 240		5.82	3.98 [f]; 3.99 [g]
*m-Cyanobenzoic	214.5 to 216		6.56	3.60 [g, k]
*p-Cyanobenzoic	219.5 to 220		6.53	3.55 [g]; 3.54 [k]
m-Dimethylamino benzoic.	151 to 152		4.89	5.1 [l]
*o-Fluorobenzoic	124 to 125		5.77	3.27 [f]
*m-Fluorobenzoic	123 to 124		5.94	3.865 [f]
*p-Fluorobenzoic	182 to 184 sb		5.61	4.14 [f]
o-Hydroxybenzoic (Salicylic).	158.5 to 159.5		7.45	3.00 [m]
m-Hydroxybenzoic	201.5 to 202.5		5.35	4.08 [g]
p-Hydroxybenzoic	214.5 to 215		4.94	4.58 [g]
*o-Iodobenzoic	161 to 162.5		6.22	2.86 [f]; 2.84 [n]
*m-Iodobenzoic	187 to 188		6.05	3.85 [f]; 3.86 [g]; 3.79 [n]
*p-Iodobenzoic	270 to 271		5.85	3.98 [n]
o-Methoxybenzoic (*o*-Anisic).	101 to 102	100.0	3.7	4.09 [f]
m-Methoxybenzoic (*m*-Anisic).	105 to 106		5.38	4.09 [f]
p-Methoxybenzoic (*p*-Anisic).	183 to 184.5		4.92	4.47 [f]
Monosubstituted benzoic acids—Continued				
	° *C*	%		
*o-Methylbenzoic (*o*-Toluic).	104 to 104.5		4.94	3.91 [f]
*m-Methylbenzoic (*m*-Toluic).	112 to 113		5.13	4.27 [f]; 4.24 [g]
*p-Methylbenzoic (*p*-Toluic).	181 to 181.5		5.03	4.37 [f]; 4.34 [g]
*o-Nitrobenzoic	147 to 148		7.44	2.17 [f]
*m-Nitrobenzoic	141 to 142.5		6.82	3.49 [f]; 3.45 [g]
*p-Nitrobenzoic	238 to 239		6.80	3.425 [f]; 3.44 [g]
Polysubstituted benzoic acids				
	° *C.*	%		
2,4-Dichlorobenzoic	163 to 164	99.9	6.55	[o] 2.76
*2,6-Dichlorobenzoic	143 to 144	99.9	7.34	[o] 1.82
3,4-Dichlorobenzoic	206 to 207	99.8	6.48	[o] 3.64
2,6-Dihydroxy-4-methylbenzoic (2,6-Dihydroxy-*p*-toluic, *p*-Orsellinic).	About 152.5 to 153.5 d.	99.9	Too great to measure	[h] 1.39; [p] 1.7
*2,6-Dimethoxybenzoic	187 to 188	99.1	4.92	[q] 3.44
*2,6-Dimethylbenzoic (2,6-Xylic).	114.5 to 115.5		5.24	[r] 3.25; [s] 3.23
3,5-Dimethylbenzoic (3,5-Xylic, Mesitylenic).	170 to 171		5.03	[r] 4.30; [h] 4.33
3,5-Dinitrobenzoic	204 to 205		8.23	[t] 2.82
*2,4,6-Trimethylbenzoic (*β*-Isodurylic, Mesitoic).	152.5 to 153.5		5.00	[r] 3.44; [h] 3.43
2,4,6-Trinitrobenzoic	216 to 223 d	99.3	Too great to measure	[t] 0.65

[a] Asterisks indicate the *meta-*, *para-*, *ortho-*, and *di-ortho*-substituted acids the log *K''* and *pK* data for which were used in calculating the equations for the four lines shown in figures 1 and 2.

[b] Determined by the capillary-tube method, using an ASTM thermometer kept at 3-in. immersion. We are in agreement with a previous report (J. F. J. Dippy and R. H. Lewis, J. Chem. Soc. **1936**, 644) that slight softening a few degrees below the melting point seems to be a property of aromatic acids. In some cases partial sublimation was evident well below the melting point. A few cases in which sublimation (sb.) or decomposition (d.) seemed especially marked are noted in the table.

[c] The percent purity stated is based on potentiometric weight titrations. In other cases the purity probably ranged from 99.5 to 100.0 percent, but 100-percent purity was assumed in making computations.

[d] *K''* is the equilibrium constant corresponding to the following equation: $A\ (\text{acid}) + B\ (\text{base}) \rightleftarrows S\ (\text{salt})$, where A is the aromatic acid in question, B is 1,3-diphenylguanidine, and S is the salt formed by the addition of A to B. It is assumed that any other form of association (such as self-association of A or B) is negligible under the conditions of the experiments.

[e] When available, recent measurements giving "thermodynamic" *pK* values are cited.

[f] Measurements by Dippy and associates, cited by J. F. J. Dippy, Chem. Revs. **25**, 151 (1939); see Table I-(3)-(a), p. 206.

[g] G. Briegleb and A. Bieber, Z. Elektrochem. **55,** 250 (1951).

[h] Critical compilation of ionization constants by J. Kendall, Int. Crit. Tables, VI, p. 259 f. (McGraw-Hill Book Co., New York, N. Y., 1929).

[i] At 17° the *K*-value 2.72×10^{-4} (≏*pK* 3.565) was obtained by L. J. Edwards, Trans. Faraday Soc. **46,** 723 (1950).

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[t] J. F. J. Dippy, S. R. C. Hughes, and J. W. Laxton, J. Chem. Soc. **1956,** 2995. The value (2.38) for 2,4,6-trinitrobenzoic acid cited by G. F. Smith and D. H. Wilkins (Anal. Chim. Acta **8,** 209 (1953)) seems to have been derived by erroneous treatment of potentiometric titration data.

vacuum oven for several hours. *Benzoic acid* was NBS Standard Sample for calorimetry and acidimetry, and *p-methoxybenzoic* (*anisic*) *acid* was NBS Standard Sample for microanalytical determination of methoxyl. *2,4,6-Trinitrobenzoic acid* was used without treatment; the purity found by titration was 99.3 percent. All other acids of commercial origin were recrystallized at least once, using decolorizing carbon to remove any colored impurities. The solvents used for recrystallization were water, aqueous ethanol, benzene, cyclohexane, or benzene-cyclohexane. Samples were dried in a vacuum oven at temperatures high enough to ensure removal of solvent without incurring the danger of anhydride-formation or substantial loss of the acid through sublimation.

b. Other Acids

m-Cyanobenzoic acid. *m*-Aminobenzoic acid was converted to *m*-cyanobenzoic by the Sandmeyer reaction [3], following essentially the procedure of Valby and Lucas [4] for preparing *p*-cyanobenzoic acid. After three recrystallizations from water (using decolorizing carbon the first two times) and intermediate extractions with benzene (which removed a little brown, insoluble material), followed by heating in a vacuum oven to about 104° C, the product (needles) melted at 214.5° to 216° C. The final recrystallization did not alter the melting point. A trace of the related antidiazotate, which is formed as a byproduct in the Sandmeyer reaction, was probably present in the final product. Others, working with much larger amounts of material and after repeated recrystallizations, have obtained products with melting points ranging from 217° to about 221° [3,5,6].

p-Cyanobenzoic acid. The synthesis of *p*-cyanobenzoic acid closely paralleled that of the *m*-isomer. The crude product was recrystallized three times from water (using decolorizing carbon) and then from benzene. After washing with cyclohexane and air-drying, the product was heated to about 65° C in a vacuum oven. The melting point was 219.5° to 220° C. Others have reported the melting point as being 218.5° to 219.0° [4,6] or 219° [7]. Our product crystallized repeatedly in the form of needles, although previous workers who have mentioned the crystalline form referred to it as microscopic leaflets [7] or plates [4].

o-Fluorobenzoic acid and *m-fluorobenzoic acid* were prepared by oxidation of the corresponding fluorotoluenes, using the procedure and molecular proportions described for the preparation of *o*-chlorobenzoic acid [8]. *2,6-Dichlorobenzoic acid* and *2,6-dimethoxybenzoic acid* were prepared as previously described [9, 10].

2,6-Dihydroxy-4-methylbenzoic (*p-orsellinic*) *acid.* The carboxyl group was introduced into orcinol (1,3-dihydroxy-4-methylbenzene) by heating it with aqueous potassium bicarbonate [11]. The product crystallized in needles from benzene; titration gave a purity of 93.1 percent, indicating that about 71 percent was present as the monohydrate. The material was then heated to about 100° C in a vacuum oven, after which its purity by titration was 99.9 percent when the sample was dissolved at room temperature on the day of the titration.[6]

3,5-Dimethylbenzoic acid was a byproduct from the preparation of nitromesitylene. It was purified by recrystallizations from aqueous ethanol, using decolorizing carbon. To prepare *2,6-dimethylbenzoic acid*, 2,6-dimethylaniline was converted to the corresponding iodoxylene by the Sandmeyer reaction. The Grignard reagent was then prepared, and carbonation was effected with "dry ice", using conventional procedures. The product was recrystallized from water. *2,4,6-Trimethylbenzoic acid* was prepared in an analogous way, starting with bromomesitylene.

3. Experimental Procedures and Results

3.1. Procedure and Apparatus

In most experiments $5\times10^{-4}-M$ stock solutions of bromophthalein magenta E (A') and of diphenylguanidine (B) were prepared, and portions were transferred to 50-ml volumetric flasks in such quantities that upon dilution to the mark the stoichiometric concentration $C_{a'}$ of bromophthalein magenta was exactly 5×10^{-5} M and the stoichiometric concentration C_b of diphenylguanidine was nC', n being 0.5 or a whole number ranging from 1 to 4. Stock solutions of the carboxylic acid (A'') were *approximately* 5×10^{-4} M, and in the final mixtures the stoichiometric concentration $C_{a''}$ was $n''C_{\mathrm{a}'}$, with n'' usually ranging from about 0.5 to about 6.[7] The K'' values reported were usually based on the results for ten different mixtures.

It seems very unlikely that for the solutions under study the presence of traces of moisture would noticeably affect the results, but all practicable measures were taken to minimize the moisture content. (1) The glassware used was thoroughly dried and thereafter stored in a desiccator or in a "dry box" maintained at about 10 to 30 percent relative humidity. (2) The benzene used for diluting solutions was boiled shortly before use and protected against moisture while cooling to room temperature. (3) Flasks containing the desired amounts of diphenylguanidine and bromophthalein magenta diluted to about one-half the final volume with benzene were heated until about 10 percent of the benzene had boiled off, and the contents were

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[6] The sample could not be brought to constant weight by repeated heatings in the vacuum oven, probably because of slight decarboxylation and sublimation during heating. A lower titer was obtained when the solution had stood overnight or had been heated to hasten dissolving of the sample. The melting point cannot be used as a criterion of purity, because softening and evolution of gas (doubtless carbon dioxide) occurs gradually. The more gradual the heating, the lower the temperature at which pronounced evolution of gas begins and the more extended the temperature range over which decomposition occurs. The melting behavior before and after oven-drying appeared to be about the same. In one experiment, a specimen of the oven-dried product showed slight shrinking from about 149°, incipient liquefaction and bubble-formation at about 152.5°, and marked liquefaction and evolution of gas at 154° to 155° C. Compare [11].

[7] Solid samples were weighed on a high-precision assay-type balance when the amount taken was less than 0.1 g.

protected from moisture while cooling.[8] (4) The stock solutions of carboxylic acids were freshly prepared each day, using vacuum-dried samples and minimizing their exposure to moist air. Solution of the samples and subsequent operations of transfer, dilution to the mark, and filling of optical absorption cells were performed in the dry box. (5) In some cases desiccant was present in the cell box during absorbance measurements.

The changes in absorbance that accompany the conversion of bromophthalein magenta E to its diphenylguanidine salt have been described previously [1 (a), (e)]. The salt has an absorption band with a maximum near 540 mμ, and none of the other reacting species dealt with in these studies shows measurable absorption at this wavelength. The absorbance at 540 mμ decreases upon the addition of a carboxylic acid, owing to the competing tendency of this acid to combine with diphenylguanidine. Measurements at 540 mμ only were used in the investigations under discussion.[9] A Beckman Model DU quartz spectrophotometer was used for transmittance measurements, the temperature being maintained at 25.0°±0.1° in most of the experiments by the use of a thermostated air bath [1(f)]. The glass-stoppered absorption cells had quartz windows and were of four lengths (2.5 mm, 5.0 mm, 10 mm, and 20 mm) [1 (a)], the cell length being so selected that usually the transmittance values were within the range 20 to 70 percent. For calculations of K'' the transmittance values were converted in the usual way to absorbance (the negative logarithm of the transmittance) values.

3.2. Experimental Data and Calculation of Association Constants

The equilibrium constants K' and K'' corresponding to eq (1) are:

$$K'=\frac{[S']}{[A'][B]}, \tag{2}$$

$$K''=\frac{[S'']}{[A''][B]}, \tag{3}$$

where the quantities in brackets signify molar concentrations of the different species in the equilibrium mixtures. B, A', and A'' were defined in section 3.1. S' and S'' refer to the diphenylguanidine salts of bromophthalein magenta E and the carboxylic acid, respectively. Of necessity the activity coefficients are all assumed to be 1, but in such dilute solutions this is a very reasonable assumption.

Applying these two equations the following expression was derived algebraically and used in calculating the K'' values:

$$K''=\frac{x-y}{y[C_{a''}-(x-y)]} \tag{4}$$

where $x=(C_a'/L)\,(nL-Z)$ and $y=(1/K')\,[Z/(L-Z)]$. Z is the absorbance of a given solution at 540 mμ per unit optical absorption cell length (here taken as 5 mm);[10] L (here taken as 1.017) is the limiting absorbance for the reaction of A' with B when C_a' is $5\times10^{-5}\,M$ and the cell length is 5 mm; K' at 25° C is taken as $2.5_5\times10^5$;[11] and the remaining symbols are as already defined in this paper.

Experimental data and the calculated K'' values for 40 acids whose association with diphenylguanidine under the stated conditions was measurable are presented in table 2.[12] The values of K'' must be regarded as provisional until factors that may affect their accuracy have been more thoroughly studied. These factors include competitive associations,[13] traces of impurities, partial adsorption of reactants on the surface of vessels,[14] and the marked sensitivity of the equilibria to minute changes in the temperature.[15] In most experiments no values were excluded in computing the average K'', but in a few cases (indicated in table 2) widely divergent values were arbitrarily excluded. Obviously, some proportions of reactants are more favorable than others for obtaining accurate results, and the best results should be obtainable with acids that nearly match bromophthalein magenta E in strength.

It is worth noting that for most of the acids the log K'' value obtained upon measuring the mixture containing each of the three components (B, A', and A'') at the stoichiometric concentration $5\times10^{-5}M$ differed by no more than 0.02 unit from the logarithm of the *average* value of K''. This suggests a quick method for obtaining a good approximation of the association constant K''.

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[8] It has been found that the absorbance measurements made after dilution to volume are unaffected by such heating, and that mixtures of these two compounds can be preserved for a long time without alteration if not too concentrated. (Crystallization of the salt occurs on standing if its concentration is as great as $5\times10^{-4}\,M$.) In later parts of the work the practice was adopted of preparing enough of these two stock solutions for several series of measurements and transferring samples to other flasks without delay (that is, before the concentrations of the stock solutions could be significantly increased by evaporation of the solvent), diluting the mixtures to about one-half of the final volume, and completing the experiments at convenience.

[9] This statement needs slight qualification. Each freshly prepared stock solution of bromophthalein magenta E was checked by dilution of a sample to $5\times10^{-5}\,M$ and measurement of the transmittance at 405 mμ; for a 2.5-mm light path this was found to be 47.1 to 47.2 percent. An additional check was made at 540 mμ on a second solution in which C_a' and C_b were both $5\times10^{-5}\,M$; with this solution in a 2.5-mm optical absorption cell a transmittance reading of 41.3 or 41.4 percent was considered acceptable.

[10] In this paper the usual symbol (A) for absorbance is replaced by the symbol Z in order to avoid confusion with the use of A in referring to acids.

[11] For this work the measurement of K' (see [1 (a) (e)]) was repeated. In doing so an attempt was made to define the L-value (formerly taken as 1.02) more precisely as well as to introduce further improvements in technique. The value of K' is very sensitive to the temperature.

[12] An example of the method of calculating (as well as of correcting) K'' is given in section 4.1, table 4.

[13] See section 4.1.

[14] For examples of such adsorption see [1(a)], p. 243 and 246, and [1(e)], p. 499.

[15] The temperature effect is being studied. The enthalpy change accompanying the reaction of bromophthalein magenta E with seven of the aromatic carboxylic acids appears to range from about 14 to about 19 kcal.

TABLE 2. *Experimental data and association constants for the reaction of aromatic carboxylic acids with 1,3-diphenylguanidine in benzene at 25° C*

$C_{a''}$[a]	n[b]	Z[c]	K''[d]
Benzoic acid			
2.543×10^{-5}	0.5	0.3388	1.71×10^{5}
2.543	1.0	.6232	1.73
5.246	1.0	.4921	1.98
10.493	1.0	.3605	1.87
5.041	2.0	.8474	1.69
10.083	2.0	.6726	1.86
15.259	2.0	.5432	1.83
10.083	3.0	.8754	1.88
15.124	3.0	.7494	1.90
20.165	3.0	.6448	1.82
Average--------	---	------	1.83×10^{5}
o-Acetoxybenzoic acid			
2.519×10^{-5}	0.5	0.2612	5.54×10^{5}
2.575	1.0	.5548	4.95
5.038	1.0	.3830	5.63
10.075	1.0	.2218	5.54
10.299	2.0	.5162	5.39
15.440	2.0	.3492	5.35
20.151	2.0	.2612	5.47
10.293	3.0	.8336	4.36
15.448	3.0	.5986	5.18
20.597	3.0	.4422	5.14
Average--------	---	------	5.26×10^{5}
o-Aminobenzoic acid			
2.519×10^{-5}	0.5	0.3796	8.09×10^{4}
2.582	.5	.3782	8.09
5.039	.5	.3206	9.58
2.519	1.0	.6632	9.02
2.582	1.0	.6688	7.84
5.163	1.0	.5798	8.87
10.077	1.0	.4724	8.88
5.163	2.0	.8684	8.70
10.187	2.0	.7514	9.39
15.280	2.0	.6632	8.81
10.187	3.0	.8996	9.64
15.280	3.0	.8314	8.51
Average--------	---	------	8.78×10^{4}
m-Aminobenzoic acid			
2.612×10^{-5}	0.5	0.3728	8.93×10^{4}
5.035	.5	.3206	9.59
2.612	1.0	.6596	9.04
5.224	1.0	.5832	8.41
10.070	1.0	.4672	9.24
5.224	2.0	.8730	7.40
10.187	2.0	.7620	8.49
15.280	2.0	.6737	8.21
20.140	2.0	.6055	8.16
15.674	3.0	.8314	8.00
20.374	3.0	.7773	7.44
Average--------	---	------	8.45×10^{4}
p-Aminobenzoic acid			
2.589×10^{-5}	0.5	0.4222	2.15×10^{4}
5.090	.5	.3772	3.83
2.528	1.0	.7130	3.20
5.057	1.0	.6708	3.01
10.179	1.0	.6178	2.53
5.057	2.0	.9070	2.59
10.356	2.0	.8566	2.65
15.269	2.0	.8134	2.61
5.178	3.0	.9578	5.05*
10.114	3.0	.9344	3.05
15.269	3.0	.9144	2.43
Average--------	---	------	2.80×10^{4}
o-Bromobenzoic acid			
2.528×10^{-5}	0.5	0.1910	1.53×10^{6}
5.056	.5	.0972	1.55
2.506	1.0	.5068	1.40
5.022	1.0	.2782	1.54
10.112	1.0	.1138	1.55
5.012	2.0	.7905	1.30
10.044	2.0	.3862	1.50
15.065	2.0	.2000	1.51
20.224	2.0	.1294	1.49
30.130	4.0	.2314	1.43
Average--------	---	------	1.48×10^{6}
m-Bromobenzoic acid			
1.250×10^{-5}	1.0	0.6502	1.12×10^{6}
2.500	1.0	.5241	0.97
2.500	1.0	.5200	1.06
2.500	1.0	.5147	1.19
3.750	1.0	.3979	1.16
5.000	1.0	.3002	1.25
6.250	1.0	.2396	1.20
7.500	1.0	.1945	1.20
10.000	1.0	.1358	1.23
12.500	1.0	.1056	1.21
15.000	1.0	.0876	1.17
20.000	1.0	.0634	1.17
5.000	2.0	.7958	1.03
10.000	2.0	.4179	1.20
12.500	2.0	.3063	1.18
Average--------	---	------	1.16×10^{6}
p-Bromobenzoic acid			
1.500×10^{-5}	0.5	0.3054	7.36×10^{5}
2.490	.5	.2381	7.88
5.042	.5	.1492	7.56
2.490	1.0	.5406	7.20
4.978	1.0	.3605	7.11
9.957	1.0	.1911	7.31
5.002	2.0	.7959	10.1*
10.004	2.0	.4908	7.09
15.126	2.0	.3072	7.20
20.008	4.0	.6289	6.85
Average--------	---	------	7.28×10^{5}
o-Chlorobenzoic acid			
2.506×10^{-5}	0.5	0.2034	1.30×10^{6}
5.048	.5	.1102	1.28
2.506	1.0	.5143	1.18
5.078	1.0	.3002	1.19
10.097	1.0	.1334	1.25
5.078	2.0	.7905	1.04
10.023	2.0	.4214	1.16
15.034	2.0	.2299	1.22
20.194	2.0	.1505	1.23
20.046	3.0	.3080	1.16
Average--------	---	------	1.20×10^{6}
m-Chlorobenzoic acid			
2.505×10^{-5}	0.5	0.2028	1.31×10^{6}
5.011	.5	.1157	1.19
2.505	1.0	.5186	1.08
5.011	1.0	.3063	1.17
10.022	1.0	.1428	1.14
10.168	2.0	.4134	1.16
15.253	2.0	.2343	1.14
20.043	2.0	.1626	1.12
15.253	3.0	.4895	1.11
20.337	3.0	.3054	1.13
Average--------	---	------	1.16×10^{6}
p-Chlorobenzoic acid			
2.542×10^{-5}	0.5	0.2441	6.95×10^{5}
5.088	.5	.1562	6.81
2.542	1.0	.5421	6.43
5.021	1.0	.3635	6.78
10.176	1.0	.1984	6.62
5.088	2.0	.7905	10.1*
10.170	2.0	.4949	6.51
15.063	2.0	.3279	6.40
20.352	2.0	.2362	6.32
20.084	3.0	.4191	6.21
Average--------	---	------	6.56×10^{5}
m-Cyanobenzoic acid			
2.527×10^{-5}	0.5	0.1367	3.82×10^{6}
5.014	.5	.0490	4.06
2.527	1.0	.4789	2.85
5.085	1.0	.1958	3.70
10.170	1.0	.0534	3.98
10.109	2.0	.2815	3.43
15.255	2.0	.0997	3.84
20.057	2.0	.0593	3.84
15.163	3.0	.3401	3.28
20.340	3.0	.1416	3.68
Average--------	---	------	3.65×10^{6}
p-Cyanobenzoic acid			
5.031×10^{-5}	0.5	0.0498	3.96×10^{6}
2.537	1.0	.4789	2.74
5.044	1.0	.2078	3.30
5.048	1.0	.2062	3.36
10.061	1.0	.0556	3.87
15.179	1.0	.0305	3.86
20.239	1.0	.0214	3.77
5.075	2.0	.7747	2.86
10.088	2.0	.2934	3.13
10.095	2.0	.2916	3.16
15.092	2.0	.1059	3.66
20.122	2.0	.0604	3.74
25.299	2.0	.0420	3.73
15.133	3.0	.3538	3.00
15.224	3.0	.3507	2.94
25.299	3.0	.0872	3.67
20.299	4.0	.4012	2.75
Average-----	---	------	3.38×10^{6}
m-Dimethylaminobenzoic acid			
2.509×10^{-5}	0.5	0.3836	7.43×10^{4}
2.509	1.0	.6688	8.21
5.139	1.0	.5916	7.89
10.270	1.0	.4882	7.70
5.135	2.0	.8706	8.31
10.277	2.0	.7680	7.88
15.405	2.0	.6820	7.67
10.277	3.0	.9070	7.61
15.405	3.0	.8404	7.53
20.073	3.0	.7766	7.71
Average-----	---	------	7.79×10^{4}
o-Fluorobenzoic acid			
2.569×10^{-5}	0.5	0.2541	5.92×10^{5}
5.035	.5	.1603	6.57
5.211	.5	.1637	6.00
2.569	1.0	.5467	5.72
5.211	1.0	.3686	5.92
5.232	1.0	.3625	6.19
10.422	1.0	.2069	5.93
10.466	1.0	.2062	5.92
5.232	2.0	.7905	7.11*
10.422	2.0	.4989	5.84
10.466	2.0	.4976	5.81
15.105	2.0	.3410	5.90
15.634	2.0	.3298	5.85
15.413	3.0	.5850	5.71
20.551	3.0	.4248	5.67
30.826	3.0	.2636	5.73
Average-----	---	------	5.91×10^{5}

TABLE 2. *Experimental data and association constants for the reaction of aromatic carboxylic acids with 1,3-diphenylguanidine in benzene at 25° C*—Continued

$C_{a''}$[a]	n[b]	Z[c]	K''[d]
m-Fluorobenzoic acid			
1.250×10^{-5}	1.0	0.6632	$5.56^{*}\times10^{5}$
1.250	1.0	.6517	10.2*
2.500	1.0	.5352	7.83
2.500	1.0	.5302	8.62
3.750	1.0	.4236	8.47
5.000	1.0	.3372	8.74
5.000	1.0	.3335	9.04
6.250	1.0	.2708	9.10
7.500	1.0	.2269	8.98
10.000	1.0	.1688	8.88
10.000	1.0	.1658	9.13
12.500	1.0	.1337	8.78
15.000	1.0	.1062	9.17
20.000	1.0	.0815	8.66
10.000	2.0	.4572	9.04
25.000	5.0	.6326	8.76
50.000	10.0	.7570	8.13
Average-----	---	------	8.76×10^{5}
p-Fluorobenzoic acid			
1.276×10^{-5}	0.5	0.3478	4.17×10^{5}
2.552	.5	.2827	3.99
5.104	.5	.1979	4.12
1.281	1.0	.6696	3.83
2.562	1.0	.5654	4.23
5.125	1.0	.4078	4.35
10.250	1.0	.2620	3.94
5.104	2.0	.8090	4.86
10.250	2.0	.5702	3.76
15.310	2.0	.4105	3.83
Average-----	---	------	4.11×10^{5}
o-Hydroxybenzoic acid			
2.535×10^{-5}	0.5	0.0553	2.97×10^{7}
5.028	.5	.0086	2.86
5.046	1.0	.0793	2.94
10.056	1.0	.0088	2.83
10.093	2.0	.1095	2.93
15.085	2.0	.0171	2.85
20.113	2.0	.0090	2.78
15.139	3.0	.1391	2.59
20.185	3.0	.0253	2.79
Average-----	---	------	2.84×10^{7}
m-Hydroxybenzoic acid			
2.504×10^{-5}	0.5	0.3224	2.27×10^{5}
5.072	.5	.2503	2.27
2.504	1.0	.6126	2.12
5.007	1.0	.4855	2.29
10.058	1.0	.3478	2.17
5.072	2.0	.8358	2.28
10.058	2.0	.6517	2.20
15.217	2.0	.5143	2.16
10.145	3.0	.8636	2.42
15.087	3.0	.7305	2.23
Average-----	---	------	2.24×10^{5}
p-Hydroxybenzoic acid			
2.541×10^{-5}	0.5	0.3876	$6.68^{*}\times10^{4}$
2.035	1.0	.6840	8.58
2.551	1.0	.6614	9.11
5.087	1.0	.5882	8.30
5.103	1.0	.5814	8.87
7.122	1.0	.5400	8.20
7.652	1.0	.5320	7.97
5.103	2.0	.8660	9.65
7.652	2.0	.8134	8.80
10.203	2.0	.7598	8.65
15.308	2.0	.6726	8.25
5.103	3.0	.9526	13.3*
12.753	3.0	.8636	9.20
17.789	3.0	.7916	8.77
Average-----	---	------	8.70×10^{4}
o-Iodobenzoic acid			
2.520×10^{-5}	0.5	0.1853	1.69×10^{6}
5.144	.5	.0889	1.73
2.520	1.0	.4989	1.64
5.168	1.0	.2636	1.62
15.431	1.0	.0628	1.68
10.336	2.0	.3585	1.63
15.122	2.0	.1858	1.68
20.574	2.0	.1164	1.65
15.504	3.0	.4248	1.56
20.163	3.0	.2518	1.62
Average-----	---	------	1.65×10^{6}
m-Iodobenzoic acid			
2.514×10^{-5}	0.5	0.2101	1.16×10^{6}
5.021	.5	.1160	1.18
5.031	1.0	.3063	1.15
10.042	1.0	.1428	1.14
15.086	1.0	.0909	1.11
10.061	2.0	.4260	1.11
15.086	2.0	.2388	1.13
20.084	2.0	.1640	1.10
15.092	3.0	.5045	1.06
20.123	3.0	.3170	1.09
Average-----	---	------	1.12×10^{6}
p-Iodobenzoic acid			
2.512×10^{-5}	0.5	0.2411	7.42×10^{5}
5.044	.5	.1518	7.29
2.512	1.0	.5432	6.61
5.044	1.0	.3546	7.27
10.063	1.0	.1915	7.15
10.087	2.0	.4841	7.22
15.131	2.0	.3116	7.00
20.126	2.0	.2261	6.90
15.075	3.0	.5680	7.02
20.126	3.0	.3993	6.87
Average-----	---	------	7.08×10^{5}
o-Methoxybenzoic acid			
2.514×10^{-5}	0.5	0.4316	$12.7^{*}\times10^{3}$
5.027	.5	.4285	7.67
10.054	.5	.4224	5.24
15.082	.5	.4076	6.00
5.022	1.0	.7352	7.60
10.044	1.0	.7212	5.46
15.067	1.0	.7122	4.39
2.508	1.5	.8972	2.20
5.016	1.5	.8850	4.40
7.524	1.5	.8826	3.28
10.032	1.5	.8754	3.44
5.006	2.0	.9320	6.69
10.012	2.0	.9268	4.08
15.018	2.0	.9194	3.65
15.022	3.0	.9656	3.23
20.030	4.0	.9790	3.37
25.037	5.0	.9842	4.29
30.044	6.0	.9870	5.30
Average-------	-------	----------	4.72×10^{3}
m-Methoxybenzoic acid			
2.516×10^{-5}	1.0	0.6091	2.21×10^{5}
5.016	1.0	.4802	2.39
5.088	1.0	.4732	2.48
7.525	1.0	.3958	2.38
10.033	1.0	.3372	2.35
10.033	2.0	.6383	2.45
10.020	3.0	.8730	2.07
[e] 1.018	1.0	.0714	3.55*
[f] 2.544	1.0	.2165	2.81
[g] 10.176	1.0	.9924	2.34
Average-------	-------	----------	2.39×10^{5}
p-Methoxybenzoic acid			
1.276×10^{-5}	0.5	0.4034	9.87×10^{4}
2.552	.5	.3726	9.22
2.520	1.0	.6632	9.01
5.040	1.0	.5934	7.96
10.126	1.0	.4868	7.92
20.252	1.0	.3830	7.00
5.040	2.0	.8684	9.37
10.081	2.0	.7744	7.68
15.122	2.0	.6898	7.49
10.074	3.0	.9070	8.17
15.110	3.0	.8428	7.68
Average-------	-------	----------	8.31×10^{4}
o-Methylbenzoic acid			
2.546×10^{-5}	0.5	0.3747	8.86×10^{4}
2.513	1.0	.6615	9.33
5.026	1.0	.5884	8.43
10.052	1.0	.4789	8.48
5.088	2.0	.8706	8.54
10.254	2.0	.7576	8.74
15.273	2.0	.6655	8.68
10.182	3.0	.9044	8.46
15.273	3.0	.8314	8.52
20.508	3.0	.7618	8.26
Average-------	-------	----------	8.63×10^{4}
m-Methylbenzoic acid			
2.503×10^{-5}	0.5	0.3570	1.27×10^{5}
2.500	1.0	.6402	1.36
5.000	1.0	.5421	1.35
10.000	1.0	.4191	1.32
5.045	2.0	.8542	1.40
10.090	2.0	.7092	1.39
15.015	2.0	.5986	1.36
10.090	3.0	.8898	1.30
15.135	3.0	.7894	1.33
20.181	3.0	.6956	1.34
Average-------	-------	----------	1.34×10^{5}
p-Methylbenzoic acid			
2.526×10^{-5}	0.5	0.3702	0.98×10^{5}
2.500	1.0	.6576	1.01
5.000	1.0	.5670	1.06
10.000	1.0	.4486	1.07
5.053	2.0	.8612	1.14
10.106	2.0	.7372	1.09
15.159	2.0	.6376	1.05
10.106	3.0	.8972	1.06
15.159	3.0	.8112	1.08
20.212	3.0	.7310	1.06
Average-------	-------	----------	1.06×10^{5}
o-Nitrobenzoic acid			
2.544×10^{-5}	0.5	0.0550	2.92×10^{7}
5.011	.5	.0084	2.96
2.533	1.0	.4597	0.64*
2.522	1.0	.4559	0.94*
5.089	1.0	.0784	2.76
10.022	1.0	.0089	2.82
10.177	2.0	.1088	2.64
15.266	2.0	.0174	2.71
20.043	2.0	.0093	2.72
15.197	3.0	.1379	2.47
20.172	3.0	.0268	2.63
Average-------	-------	----------	2.74×10^{7}

TABLE 2. *Experimental data and association constants for the reaction of aromatic carboxylic acids with 1,3-diphenylguanidine in benzene at 25° C*—Continued

$C_{a''}$[a]	n[b]	Z[c]	K''[d]
m-Nitrobenzoic acid			
1.250×10^{-5}	0.25	0.0698	8.14×10^{6}
1.250	.5	.2468	10.4*
2.501	.5	.1095	6.90
1.251	1.0	.6345	8.88*
2.503	1.0	.4647	6.16
3.754	1.0	.2933	6.03
5.015	1.0	.1558	6.88
5.015	1.0	.1581	6.65
7.522	1.0	.0613	6.52
10.030	1.0	.0356	6.49
5.024	2.0	.7724	6.75
10.140	2.0	.2124	6.64
15.210	2.0	.0660	6.38
15.080	3.0	.2718	6.06
20.107	3.0	.0962	6.29
20.047	4.0	.3072	6.25
25.058	4.0	.1232	6.26
[f] 2.507	1.0	.0725	7.43
[g] 10.108	1.0	.3239	6.32
Average--------	-------	----------	6.60×10^{6}
p-Nitrobenzoic acid			
2.560×10^{-5}	0.25	0.0295	6.36×10^{6}
2.559	.5	.1084	6.42
5.121	.5	.0332	6.28
2.559	1.0	.4535	7.45*
5.118	1.0	.1527	6.43
10.242	1.0	.0358	6.19
10.237	2.0	.2107	6.29
15.363	2.0	.0666	6.14
15.356	3.0	.2522	6.11
Average--------	-------	----------	6.28×10^{6}
2,4-Dichlorobenzoic acid			
2.507×10^{-5}	0.5	0.1404	3.66×10^{6}
4.975	.5	.0531	3.72
5.009	1.0	.2028	3.62
9.950	1.0	.0601	3.60
15.041	1.0	.0332	3.56
10.018	2.0	.2827	3.59
12.534	2.0	.1616	3.62
14.925	2.0	.1091	3.63
20.036	2.0	.0639	3.54
19.900	3.0	.1580	3.41
25.045	3.0	.0939	3.45
Average--------	-------	----------	3.58×10^{6}
2,6-Dichlorobenzoic acid			
2.593×10^{-5}	0.5	0.0596	2.18×10^{7}
5.186	.5	.0099	2.32
2.593	1.0	.4397	1.59*
5.016	1.0	.0952	2.12
7.779	1.0	.0190	2.27
10.031	2.0	.1310	2.19
15.047	2.0	.0224	2.17
20.743	2.0	.0102	2.31
15.047	3.0	.1668	1.94
20.063	3.0	.0340	2.08
Average--------	-------	----------	2.18×10^{7}
3,4-Dichlorobenzoic acid			
2.513×10^{-5}	0.5	0.1479	3.17×10^{6}
5.025	.5	.0602	3.11
5.025	1.0	.2159	3.04
10.151	1.0	.0662	3.09
12.674	1.0	.0506	2.90
12.674	2.0	.1792	2.96
15.226	2.0	.1213	3.00
20.302	2.0	.0738	2.93
20.278	3.0	.1700	2.89
25.126	3.0	.1095	2.84
Average--------	-------	----------	2.99×10^{6}
2,6-Dimethoxybenzoic acid			
2.546×10^{-5}	0.5	0.3836	7.31×10^{4}
2.546	1.0	.6688	8.02
5.093	1.0	.5814	8.90
10.010	1.0	.4822	8.32
5.093	2.0	.8684	9.07
10.185	2.0	.7640	8.34
15.015	2.0	.6764	8.30
10.010	3.0	.9070	8.36
15.015	3.0	.8336	8.68
20.020	3.0	.7680	8.28
Average--------	-------	----------	8.36×10^{4}
2,6-Dimethylbenzoic acid			
2.509×10^{-5}	0.5	0.3316	1.96×10^{5}
2.509	1.0	.6214	1.83
5.049	1.0	.5130	1.75
10.037	1.0	.3696	1.87
5.049	2.0	.8474	1.68
10.097	2.0	.6802	1.75
15.056	2.0	.5530	1.77
20.075	2.0	.4584	1.82
10.097	3.0	.8850	1.47
15.146	3.0	.7660	1.64
Average--------	-------	----------	1.75×10^{5}
3,5-Dimethylbenzoic acid			
2.527×10^{-5}	0.5	0.3688	1.01×10^{5}
2.527	1.0	.6502	1.12
5.069	1.0	.5664	1.04
7.582	1.0	.4960	1.09
5.055	2.0	.8590	1.21
10.137	2.0	.7350	1.10
15.206	2.0	.6394	1.03
20.115	2.0	.5714	0.99
15.164	3.0	.8134	1.05
20.115	3.0	.7392	1.01
Average--------	-------	----------	1.06×10^{5}
3,5-Dinitrobenzoic acid			
2.594×10^{-5}	0.5	0.0188	1.67×10^{8}
5.189	1.0	.0236	1.67
6.347	1.0	.0054	1.71
7.507	1.0	.0028	1.86
7.616	2.0	.4414	0.29*
10.377	2.0	.0288	1.66
15.013	2.0	.0030	1.72
15.566	3.0	.0318	1.60
17.771	3.0	.0084	1.64
22.520	3.0	.0031	1.67
Average--------	-------	----------	1.69×10^{8}
2,4,6-Trimethylbenzoic acid			
2.528×10^{-5}	0.5	0.3688	1.01×10^{5}
2.528	1.0	.6632	0.90
5.060	1.0	.5664	1.05
10.113	1.0	.4524	1.02
5.060	2.0	.8612	1.14
10.119	2.0	.7474	0.99
15.170	2.0	.6412	1.03
10.113	3.0	.9044	0.87
15.179	3.0	.8134	1.05
20.239	3.0	.7372	1.01
Average--------	-------	----------	1.01×10^{5}

[a] Stoichiometric concentration of the aromatic carboxylic acid. All concentrations are expressed in moles per liter of solution.

[b] C_b (stoichiometric concentration of diphenylguanidine) $= n.C^{a'}$ (where $C^{a'}$ is the stoichiometric concentration of bromophthalein magenta E). $C^{a'}$ is $5\times10^{-5}M$ in all experiments except where otherwise indicated.

[c] Z (absorbance) $= -\log T$ (transmittance). In this paper the usual symbol (A) for absorbance is replaced by the symbol Z to avoid confusion with the use of A in referring to acids. The values given for Z are for the wavelength 540 mμ, per 5-mm cell length. Four decimal places were retained to avoid computational errors.

[d] K'' is the equilibrium constant for the reaction: B (diphenylguanidine) $+ A''$ (aromatic carboxylic acid) $\rightleftarrows S''$ (diphenylguanidinium salt of the aromatic carboxylic acid) in benzene at 25° C. See section 3.2 for the mathematical expression used and the assumptions made in computing K''. Values marked with an asterisk were omitted in averaging. Note that the values of K'' given in this column were computed on the assumption that the aromatic carboxylic acid (A'') was entirely in the monomeric form. See section 4.1 for discussion and for "corrected" K'' values for some of the acids.

[e] $C^{a'} = 10^{-5}\ M$.

[f] $C^{a'} = 2.5\times10^{-5}\ M$.

[g] $C^{a'} = 10^{-4}\ M$.

4. Discussion of Results

4.1. General Discussion of the Method

It is readily apparent that the relative strengths of different acids in a solvent as inert as benzene cannot be measured without the addition of a *reference base*. The choice of diphenylguanidine as the reference base was made after tests of numerous basic indicator dyes (in the form of the free base) showed that none possessed adequate solubility, stability, and reactivity.[16] In using diphenylguanidine, an indicator *acid* must be present. The acid selected was bromophthalein magenta E (tetrabromophenolphthalein ethyl ester), whose association in benzene solution with diphenylguanidine and with di-*o*-tolylguanidine has been studied in detail in this laboratory [1(a) (e), (f)]. The feasibility of assessing at least semiquantitatively the relative strengths of a large variety of organic acids in benzene, including acids as weak as acetic and benzoic acids, by measuring the ab-

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[16] To be suitable for our purposes the base had to be fairly strong. This meant that it had to be sought among the strongest aliphatic amines or among the available guanidines, amidines, or their vinylogs. The indicator bases tested included members of the azo, azine, oxazine, and thiazine families of dyes, as well as anhydro-bases of the triphenylmethane group. A large proportion of the dyes were found to be too easily affected by light or too susceptible to attack by atmospheric moisture, oxygen, or acidic vapors. Others were of adequate stability, but reacted measurably only with acids of pK about 3 or less, and even in such cases a very large excess of the acid was usually required.

sorbance of very dilute solutions containing bromophthalein magenta E, the organic acid in question, and either diphenyl- or ditolylguanidine, all present at approximately the same stoichiometric concentration, was shown in exploratory studies made about twelve years ago.[17] Diphenylguanidine was selected in preference to di-*o*-tolylguanidine chiefly because its reactivity as a base in benzene (which is less than that of di-*o*-tolylguanidine [1 (a), (e), (f)]) was thought to be more suitable for the experiments contemplated.

The scheme adopted for this investigation has the disadvantage that any errors in the two constants L and K' (see section 3.2) will be reflected in the values obtained for K'', and still further study may result in slight modifications of these two values. However, this would cause little difference in the relative orders of strength.

The possibility of competitive associations must be kept in mind in planning and interpreting studies of acid-base equilibria in benzene as a solvent. Cryoscopic measurements have provided evidence that the base diphenylguanidine is intermolecularly associated to some extent, by hydrogen bonding, when dissolved in naphthalene [12] or benzene [13], but at room temperature and the low concentrations used in this work any error from this source may be presumed to be negligible. Intermolecular association of bromophthalein magenta E has not been observed, and is not to be expected [1 (a), p. 232].

On the other hand, the tendency for the molecules of carboxylic acids to associate in pairs, whether in the gaseous, liquid, or solid states or dissolved in a solvent like benzene, is a well-known manifestation of hydrogen bonding. At very high concentrations, still larger aggregates of molecules may exist. In dilute solutions, however, as shown by experimental studies (mostly of benzene solutions) reported within the last 15 years,[18] there appears to be an equilibrium between double and single molecules.

Information on the dimer $\rightleftarrows$ monomer equilibrium of benzoic acid and its derivatives is still very fragmentary, as is evident from an inspection of table 3. This table is a compilation of the available equilibrium constants K_{21} (corresponding to the equation $A_2 \rightleftarrows 2A$), converted where necessary to the same units of concentration (moles per liter) as those used in the work presented in this paper. Additional K_{21} values for 5.5°, 25°, and 30° C were computed in cases where K_{21} data for several temperatures were available, and are included in table 3. At 25° C most of the K_{21} values are in the range from about 1.4×10^{-3} to about 3.7×10^{-3}. *o*-Methoxybenzoic acid is a striking exception, showing only a slight tendency to become dimeric.[19] The K_{21} value reported for *p*-methoxybenzoic acid is about the same as K_{21} for benzoic acid, but the values that have been reported for *p*-fluorobenzoic and *p*-toluic acids indicate an appreciably greater tendency to dimerize.[20]

The experimental work involved in this survey was designed to yield comparative K'' values that would be reliable, at least as rough approximations, without taking the dimer-monomer equilibria of the carboxylic acids into account. It was thought that this objective could be achieved by keeping all of the concentrations low and using not greatly differing stoichiometric proportions of the three reacting components (see table 2). In one case—that of benzoic acid—an additional detailed study of the equilibria at 25° C was made in which stoichiometric concentrations of this acid ranging from one-half to as much as twenty times that of bromophthalein magenta E were used. The data of this experiment were used in calculating uncorrected values of K'' and also in correcting K'' values by taking apparent dimer contents of solutions into consideration. The steps following in making the calculations are shown in detail in table 4. In the last column of this table are given the corrected K'' values obtained when K_{21} was assigned the value 1.9×10^{-3}. This is the K_{21} value considered to best fit the data after all of the values of $K_{21}(\times 10^3)$ ranging from 1.1 to 3.0 by 0.1 increments had been tried and in each case the average deviation from the mean value of K'' had been computed. The value of K_{21} adopted is close to the values obtained by others from ebullioscopic, distribution, and isopiestic measurements (see table 3).[21] The mean value of K'' given in table 4 exceeds by about 14 percent the mean value given in table 2, but the difference would have been only 5 percent if three rather low values of K'' had been excluded in computing the average value given in table 2 and the remaining values had been corrected as in table 4.

In an analogous manner the K'' values of table 2 were corrected in the cases of *o*-chloro-, *m*-iodo-, and *p*-methoxybenzoic acids and the three toluic acids, using the K_{21} values given in table 3. This treatment brought about slightly increased precision of the results for *o*-toluic acid and *m*-iodo- and *p*-methoxybenzoic acids, but slightly reduced precision for the other three cases.[22] Increases of from 2.5 to 6.0 percent in the values of K'' also resulted.

In the discussion so far it has been assumed that the diphenylguanidine salts of bromophthalein magenta E and the various carboxylic acids all have the composition BA. Studies reported earlier [1(a),(e)] justify this assumption with respect to the diphenylguanidine salt of bromophthalein magenta E. However, the possibility of additional struc-

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[17] Such experiments were referred to in [1 (a), p. 261].

[18] A recent comprehensive article on the association of carboxylic acids includes a summary and discussion of such studies [14].

[19] It should be pointed out that the data for this acid were derived from distribution measurements, so that the K_{21} value refers to water-saturated benzene solutions. In some cases it is very probable that the dimer-monomer equilibrium is affected by the presence of water. However, in the case of *o*-methoxybenzoic acid the conclusion of a low dimer content is substantiated by infrared data, which indicate that a relatively strong intramolecular hydrogen bond stabilizes the monomeric form of this acid [15, 16]. Intramolecular hydrogen bonding (that is, chelation) has also been suggested as explaining the comparatively high K_{21} value for *o*-fluorobenzoic acid (table 3, footnote j). The data of table 3 suggest that the other *o*-halogenated acids may also be chelated to a substantial degree in benzene. A different explanation—steric hindrance—was suggested to account for the relatively large value of K_{21} for *o*-toluic acid in comparison with the K_{21} values for benzoic and *m*-toluic acids (footnote g, table 3).

[20] Several investigators have pointed out that there seems to be a rough correlation between the tendency for carboxylic acids to exist in the monomeric state in benzene and their tendency to ionize in aqueous solution. The correlation is very imperfect, and there appear to be two separate relations for carboxylic acids—one covering acids in which there may be resonance between R— and —COOH (for instance, benzoic, cinnamic, and phenylpropiolic acids), and a second relation covering acids in which such resonance is not possible (for example, fatty acids) [14].

[21] According to A. A. Maryott, the electric polarization method, for reasons not understood, seems to give anomalous K_{21} results for benzoic acid (see table 3, footnote i).

[22] The measure of precision referred to here was the average deviation from the mean value of K''.

TABLE 3. *Dissociation constants (K_{21}) of dimeric benzoic acids in benzene* [a]

Temperature [b]	$(10^3)K_{21}$												
	Substituent												
	None	*o*-Br	*o*-Cl	*o*-F	*m*-F	*p*-F	*o*-OH	*m*-I	*o*-OCH$_3$	*p*-OCH$_3$	*o*-CH$_3$	*m*-CH$_3$	*p*-CH$_3$
°*C*													
5.5	[c] 0.572 [d] (.692) [e] .18 [f] .64 [g] (.596)	[c] 1.07	[d] (1.377)	------	------	------	----	[d] (0.974)	------	[d] (0.648)	[g] (0.873)	[g] (0.445)	[d] (0.145)
25	[d] (1.76) [f] (2.0) [g] (1.61) [h] 1.9	------	[d] (3.73)	------	------	------	----	[d] (2.43)	[f] (350)	[d] (1.80)	[g] (2.37)	[g] (1.37)	[d] (0.415)
30	[d] (2.18) [g] (2.04) [i] 5.3	------	[d] (4.72)	[j] 5.2	[j] 0.56	[j] 0.78	----	[d] (3.00)	[f] (370)	[d] (2.28)	[g] (2.99) [k] 2.44	[g] (1.78) [k] 2.00	[d] (0.531)
32	------	------	------	------	------	------	----	------	------	------	------	[g] 1.97	------
32.5	[g] 2.30	------	------	------	------	------	----	------	------	------	[g] 3.38	------	------
35	[f] 2.7	------	------	------	------	------	----	------	------	------	------	------	------
40	[f] 3.2	------	------	------	------	------	[f] 95	------	[f] 436	[f] 4.67	------	------	------
43.5	[g] 3.69	------	------	------	------	------	----	------	------	------	[g] 5.43	[g] 3.45	------
48	------	------	------	------	------	------	----	------	------	[d] 6.40	------	------	------
50	------	------	------	------	------	------	----	------	[f] 499	[f] 7.55	------	------	------
54	[d] 5.59	------	[d] 12.8	------	------	------	----	[d] 7.64	------	------	------	------	[d] 1.53
56.5	[g] 6.33	------	------	------	------	------	----	------	------	------	[g] 9.27	[g] 6.31	------
60	------	------	------	------	------	------	----	------	[f] 577	[f] 11.7	------	------	------
61	------	------	------	------	------	------	----	------	------	[d] 8.44	------	------	------
65.5	[d] 8.54	------	[d] 20.5	------	------	------	----	[d] 11.0	------	------	------	------	[d] 2.44
70	------	------	------	------	------	------	----	------	[f] 740	[f] 19.0	------	------	------
80	[d] 13.6 [e] 9.7	------	[d] 33.5 [e] 28	------	------	------	[e] 56	[d] 18.4	------	[d] 16.5	------	------	[d] 4.20

[a] K_{21} corresponds to the equation $A_2 \rightleftarrows 2A$, and equals $(2\alpha^2 C_a)/(1-\alpha)$. All K_{21} values cited in this table are on the *molar* basis, conversion having been made where necessary by using the relations, K (*molar*) $= K$ (*molal*) $\times d_4^t$ (benzene) $= K$ (*mole fraction*) $\times 100_4^t/78.11$. Parentheses surrounding a K_{21} value signify that it was derived by interpolation or extrapolation. The experimental procedures used in measuring K_{21} are indicated in footnotes c to k.

[b] In some cases temperatures given in the original articles have been rounded off to the nearest degree or half-degree.

[c] B. C. Barton and C. A. Kraus, J. Am. Chem. Soc. **73**, 4561 (1951). (Cryoscopic.)

[d] G. Allen and E. F. Caldin, Trans. Faraday Soc. **49**, 895 (1953). (Ebullioscopic.)

[e] K. L. Wolf and G. Metzger, Ann. Chem. Liebigs **563**, 157 (1949). (Cryoscopic or ebullioscopic.)

[f] M. Davies and D. M. L. Griffiths, J. Chem. Soc. **1955**, 132. (Mostly distribution.)

[g] F. T. Wall and F. W. Banes, J. Am. Chem. Soc. **67**, 898 (1945). (Isopiestic.)

[h] M. M. Davis and M. Paabo. See section 4.1 of this paper. (Spectral absorption in the visible region.)

[i] H. A. Pohl, M. E. Hobbs, and P. M. Gross, J. Chem. Phys. **9**, 408 (1941). (Electric polarization.)

[j] A. A. Maryott, M. E. Hobbs, and P. M. Gross, J. Chem. Phys. **9**, 415 (1941). (Electric polarization.)

[k] A. A. Maryott, M. E. Hobbs, and P. M. Gross, J. Am. Chem. Soc. **71**, 1671 (1949). (Electric polarization.)

tures—in particular, the structure BA_2—for the carboxylic acid salts of diphenylguanidine must be considered. In fact, spectrophotometric evidence of such a structure was obtained in five experiments using indicator bases mentioned above (see footnote 16) mixed with different carboxylic acids.[23] But these were all cases in which the stoichiometric concentrations of acid had to be much greater than that of the indicator base (from a few hundred to several thousand times as great) for measurable changes in spectral absorption to occur; and in experiments with a very strong carboxylic acid in which only about five times as much acid as base was required, a salt of the structure BA appeared to be formed.

From the data of tables 2 and 4 and the above discussion, it seems justifiable to infer that dimerization of the carboxylic acid is the only competitive reaction of importance in the dilute solutions dealt with in this paper and that neglecting this source of error (as will be done in the subsequent discussion) does not invalidate the general conclusions reached. Still further justification is provided by a statistical analysis of the data for six of the acids, made by W. J. Youden of the Bureau. For these acids (which were the *o*-amino, *o*-fluoro, *o*-methoxy, *m*-bromo, *m*-nitro, and *p*-cyano derivatives of benzoic acid), there was no demonstrable connection between individual values derived for K'' and the concentrations employed.

In future work, however, it would be well to attempt to deduce K_{21} as well as K'', as illustrated in table 4, by working with somewhat larger con-

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[23] Evidence of a similar nature has been obtained by others from conductance titrations of amines with carboxylic acids [17] and from cryoscopic measurements of amine-carboxylic acid mixtures [18] in benzene, as well as from infrared measurements of triethylamine-acetic acid mixtures in carbon tetrachloride [19]. In the last-mentioned case the authors concluded, for example, that 0.1-M acetic acid half-neutralized with triethylamine contains mainly a stable salt of the structure BA_2 which, upon further additions of triethylamine up to a concentration about twice that of the acetic acid, is gradually converted to the salt BA.

TABLE 4. *Calculation of K'', uncorrected and corrected, for the association of benzoic acid with diphenylguanidine in benzene at 25° C* [a]

n	$C_{a''}$	Z	$\frac{[S']}{[A']}$ [b]	$[B]$ [c]	$(5/L)(nL-Z)$	$[S'']$ [d]	$[A'']$ [e]	$\frac{[S'']}{[A'']}$	$K''_{\text{uncor.}}$ [f]	α [g]	$K''_{\text{cor.}}$ [g]
0.5	2 500$\times10^{-5}$	0.3344	0.4899	0.1921$\times10^{-5}$	0.8559$\times10^{-5}$	0.6638$\times10^{-5}$	1.836$\times10^{-5}$	0.3615	1.88$\times10^{5}$	0.987	1.90$\times10^{5}$
.5	5.000	.2629	.3486	.1367	1.2074	1.071	3.929	.2726	1.99	.963	2.07
.5	9.993	.1900	.2297	.0901	1.5657	1.476	8.517	.1733	1.92	.925	2.08
.5	24.983	.1088	.1198	.0470	1.9649	1.918	23.06	.0832	1.77	.837	2.11
1.0	2.500	.6162	1.537	.6028	1.9703	1.368	1.132	1.208	2.00	.998	2.00
1.0	5.000	.5031	0.9790	.3840	2.5263	2.142	2.858	0.7495	1.95	.975	2.00
1.0	10.000	.3655	.5610	.2200	3.203	2.983	7.017	.4251	1.93	.935	2.06
2.0	10.000	.6676	1.911	.7495	6.715	5.966	4.034	1.479	1.97	.962	2.05
2.0	15.000	.5421	1.142	.4479	7.335	6.887	8.113	0.8489	1.90	.927	2.05
2.0	25.064	.3952	0.6356	.2493	8.057	7.808	17.26	.4524	1.81	.864	2.09
2.0	30 073	.3506	.5261	.2063	8.274	8.068	22.00	.3667	1.78	.832	2.12
2.0	40.028	.2884	.3958	.1552	8.583	8.428	31 60	.2667	1.72	.790	2.18
2.0	50.035	.2564	.3371	.1322	8.741	8.609	41.43	.2078	1.57	.755	2.08
2.0	60.101	.2261	.2859	.1121	8.888	8.776	51.32	.1710	1.53	.720	2.12
3.0	15.000	.7447	2 735	1.0725	11.336	10.263	4.737	2.167	2.02	.953	2.12
3.0	20.000	.6402	1.699	0.6663	11.852	11.186	8.814	1.269	1.90	.922	2.06
3.0	40.097	.4193	0.7015	.2751	12.939	12.66	27.44	0.4614	1.68	.809	2.08
3.0	50.035	.3629	.5548	.2176	13.214	13.00	37.04	.3510	1.61	.770	2.09
3.0	60.101	.3220	.4633	.1817	13.416	13 23	46.87	.2823	1.55	.735	2.11
3.0	80.134	.2688	.3593	.1409	13.676	13.54	66.59	.2033	1.44	.680	2.12
3.0	100.168	.2311	.2941	.1153	13.863	13.75	86.42	.1591	1.38	.635	2.17
Average											2.08$\times10^{5}$

[a] Provisional values obtained by M. M. Davis and M. Paabo. See the discussion in section 4.1, and also see section 3.2 for the meaning of the symbols, the value of L and of K', and the method of calculating K''_{uncor}. All concentrations are in moles per liter.

[b] Z divided by L-Z gives $[S']/[A']$. Four decimal places were retained in the Z values to avoid computational errors.

[c] $[S']/[A']$ multiplied by $1/K'$ gives $[B]$.

[d] Column 6 minus column 5.

[e] Column 2 minus column 7.

[f] See eq (3), section 3.2.

[g] The values of α were calculated from the eq $K_{21}=(2\alpha^2C_a)/(1-\alpha)$, assuming the value of K_{21} to be 1.9×10^{-3} (moles per liter) and substituting the various values in column 8 of this table for C_a. $K''_{\text{cor.}}$ (column 12) was then obtained by dividing $K''_{\text{uncor.}}$ by the corresponding value of α.

centrations of the carboxylic acids than those employed in most of this investigation.[24]

4.2. Comparative Strengths in Benzene and Water

Experimental work of recent years has shown clearly that the comparative reactivities of a series of acids in a nonionizing medium like benzene, as expressed by the *equilibrium constants for association* with a suitable reference base, should parallel the customary indexes of acidic reactivity in water, namely, the *ionic dissociation constants* [1]. This means, of course, that when ionic dissociation constants are expressed as pK (-log $K_{\text{dissocn.}}$) values, there should be an *inverse parallelism.* However, in water secondary phenomena (solvation, ionization) accompany the fundamental acid-base reaction eq(1), while in comparatively inert solvents like benzene various manifestations of hydrogen-bonding (for instance, chelation) become prominent. For such reasons, occasional deviations from a linear relationship between the two sets of equilibrium constants are to be expected.

a. Effects of Substituents on the Strength of Benzoic Acid

In considering the deviations observed in this investigation, it is necessary to have in mind current views as to how the nature and position of substituents account for the relative strengths of substituted benzoic acids. The following summary may be helpful to readers who are unfamiliar with recent developments in this area:[25]

(1) A substituent influences the strength of a carboxylic acid RCOOH according to its electron-attractive nature and its proximity to the —COOH group. Replacement of hydrogen atoms in the *R*-radical by atoms or groups that are more electron-attractive causes the electrons of the H—O linkage to be brought more under the control of the oxygen, thus facilitating the removal of the carboxylic proton. Some common substituents exhibit the following order of decreasing electron-attractive character:

$$NO_2>F>Cl>Br>I>OH>C_6H_5>H>CH_3$$

As the list indicates, most groups are more electron-attractive than hydrogen, and thus their substitution for hydrogen usually results in increased acidity, but the methyl group is less electron-attractive and can be expected to reduce the acidity.

(2) The electrical effect of the substituent is considered to be transmitted partly through space (or through the solvent) and partly through the molecule. The directly transmitted influence is known as the "field effect", and the influence transmitted through the molecule by relay from atom to atom is commonly referred to as the "inductive effect". Both effects operate in the same direction and fall off with increasing distance of the substituent from the —COOH group, the latter effect more rapidly than the former. They have often been treated as a single influence.[26]

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[24] Lack of information about the dimer-monomer equilibria of the carboxylic acids concerned is likely to have been the principal reason for the failure of some earlier attempts to formulate quantitatively acid-base equilibria in benzene and in chloroform by spectrophotometric [20] and polarimetric [21] measurementsl Those experiments employed stoichiometric concentrations of base and acid far. arger than any used in this work. Other kinds of competitive associations may also have been involved.

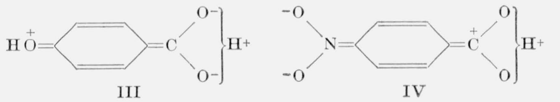
[25] References [22] to [28], on which this summary is based, furnish more rigorous and detailed discussions of the effect of structural factors on acidic strengths, including the historical development of the ideas currently accepted, some recent experimental observations, and many additional references.

[26] Some recent efforts to disentangle the two effects are discussed in [28].

(3) In addition to the above effects, resonance (mesomeric) effects are important in benzoic acid and substituted benzoic acids. Several factors seem to be involved.

In benzoic acid itself, resonance is believed to have an acidity-reducing effect. This can be attributed to a reduction in the stability of the benzoate ion, as suggested in formulas I and II. That is, in resonance form II the carboxylate group is conjugated with the benzene ring. This increases the negative charge on the oxygens, thus making the —COOH proton less easily removed.

Resonance of the benzoate ion among forms like I and II can be either reinforced or opposed by substituting groups such as —OH, —OCH_3, —NH_2, —NO_2, and —CN in the *ortho* and *para* positions. These are all groups that can become conjugated with the ring—the first three by releasing electrons and the last two by acquiring electrons, as exemplified in formulas III and IV, respectively. As the formulas indicate, an —OH group in the *para* position reinforces, but a —NO_2 group opposes, the kind of acid-weakening resonance of the —COO— group with the ring which was illustrated in formula II. In III resonance opposes the acid-strengthening inductive and field effects of the substituent (—OH), but in IV it reinforces these effects. The —OCH_3 and —NH_2 groups resemble —OH, while —CN resembles —NO_2 in resonance behavior. Substituents do not become involved in such resonance when in the *meta* position, and their influence is then ascribed wholly (or almost wholly) to inductive and field effects.



A bulky substituent located close to the —COOH group, as in *o*-substituted benzoic acids, can prevent the nearly coplanar alinement of the phenyl and carboxyl groups thought to be essential for the kind of resonance indicated in formulas II to IV. This "steric inhibition of resonance" has been proposed as an explanation for such phenomena as the substantial increase in the ionization of *o*-toluic acid (pK=3.91) over that of benzoic acid (pK=4.20). Actually, as indicated above under 4.2.a(1), a —CH_3 group would be expected to *reduce* the strength of benzoic acid when in the *ortho* position—just as it does when in the *meta* or *para* position, but to an even greater degree.

(4) Finally, hydrogen bonding appears to affect the strengths of certain benzoic acids with *ortho* substituents, in some cases having an acid-strengthening effect and in others, a weakening effect. Thus, in accounting for the relatively great strength of salicylic acid (pK=3.00), it has been suggested that the anion is stabilized by the formation of a chelate ring in which the *phenolic hydrogen* is bonded to a *carboxylate oxygen* [29]. The still greater strengths of γ-resorcylic (2,6-dihydroxybenzoic) and *p*-orsellinic acids can be explained along similar lines [30].[27] On the other hand a tendency for bonding between the carboxylic hydrogen and an *ortho* substituent (see footnote 19) would reduce the tendency to ionize and react in other ways as an acid.

In large measure the ideas just summarized were founded on the ionic behavior of the acids in water, although other observations, such as the effects of substituents on the rates of various organic reactions, were also taken into account.

b. *meta*-Substituted Benzoic Acids

In applying these views to the equilibrium studies dealt with here, one will naturally expect to find that the *meta*-substituted benzoic acids, in which electrical influences of substituents seem to be transmitted to the —COOH group with little if any complication by resonance, steric hindrance, and hydrogen bonding, are the acids showing the most constancy in the order of relative strengths in the two solvents, benzene and water. Actually, as shown in figure 1, the relative order of strength in the two solvents was found to be preserved very exactly for nine of the *meta*-substituted acids investigated.[28] Figure 1 was prepared by using the log K'' and pK values for *meta*-substituted acids compiled in table 1. The equation for the line, which was computed by the least squares method using the log K'' and pK values for the seven *meta*-substituted acids designated by asterisks, is

$$pK = -0.461 \log K'' + 6.623. \tag{5}$$

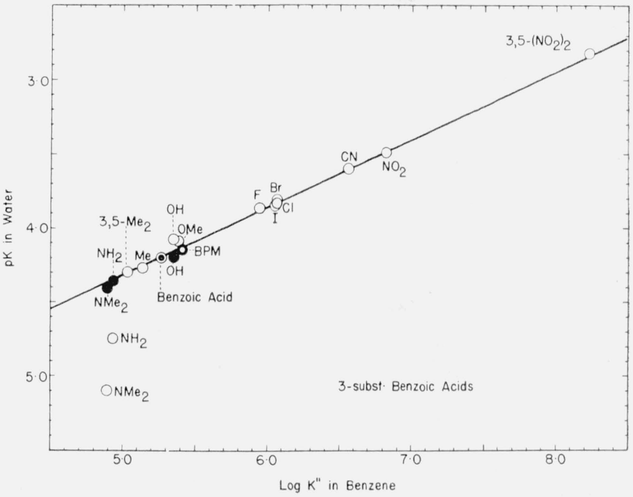


FIGURE 1. *Comparison of the strengths of 3-substituted benzoic acids in benzene and water, as measured by log K'' and pK, respectively; t=25° C.*

Open circles, *experimental* pK values plotted against log K'' values. Solid circles, pK values *calculated* using Hammett σ values plotted against log K'' values.

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[27] A similar explanation has been offered for the anomalously great ionization of *o*-toluic acid in water, but steric inhibition of resonance is now considered a more probable explanation.

[28] Note the open circles only.

Benzoic acid and bromophthalein magenta E may be added to this group of acids.[29]

It seems reasonable to consider the line as a standard or "norm" for the behavior of benzoic acids in comparisons employing log K'' and pK as the measures of acidity. Points falling above this line then refer to acids that appear to be too strong in water or too weak in benzene to conform to standard behavior, while the reverse is true for points located below the line. Four of the *meta*-substituted acids deviate significantly from standard behavior—for two of them (m-OH and m-OCH_3) the points are a little above the standard line, and for the other two (m-NH_2 and m-$N(CH_3)_2$) the points are substantially below the line. These cases are referred to again at the end of this section.

A very similar figure would have been obtained by plotting the Hammett *sigma* values against log K''. The σ values, as is well known, are obtained from the relationship known as "Hammett's equation":

$$\log k - \log k^{\circ} = \rho\sigma. \qquad (6)$$

Equation (6) was shown by Hammett to be applicable in a great many cases as an expression of the electrical effects of single *meta* or *para* substituents on rates as well as equilibrium constants of side-chain reactions of benzene derivatives [31,32]. Additional examples are continually being discovered. By definition, k is a reaction rate or equilibrium constant for a compound with a *meta* or *para* substituent, k° is the corresponding constant for the parent (unsubstituted) compound, ρ is a *reaction* constant that is constant for all substituents in any given reaction series under fixed reaction conditions (temperature, medium), and σ is a *substituent* constant determined only by the nature of the *meta* or *para* substituent. As the most convenient way of devising a numerical scale of σ values, ρ for the ionization of benzoic acids in water at 25° C was arbitrarily assigned the value 1 [31]. The σ values (with a few exceptions) are then obtained by making the appropriate substitutions in eq (6). It is evident from eq (6) that the substituents which most augment the acidity of benzoic acid have the most positive σ values. For other reaction series ρ can be obtained by plotting log k (customarily as the ordinate) against σ [31]. The slope of the best straight line through the points is the value of ρ. Applying this procedure to the reaction of diphenylguanidine with the "standard" *meta*-substituted benzoic acids in benzene yields 2.17 as the value for ρ.[30]

In terms of electron theory, the quantity ρ measures the susceptibility of a given reaction to a change in electron density at the reaction site. Positive and negative values of ρ indicate reactions facilitated by low and high electron density, respectively. As indicated above, the values of σ for various substituents measure their capacities to cause changes in electron density at the reaction site [31,32].

Hammett did not derive the σ values for m- and p-NH_2 from the aqueous ionization constants of the aminobenzoic acids, but rather from published data on the alkaline hydrolysis of the ethyl benzoates in 87.83 percent ethanol at 30° ([31 (d)], table I). Using the σ value so obtained (-0.161) and eq (6) to *calculate* the pK for m-aminobenzoic acid gives the value 4.36. The point located by plotting this pK value against our log K'' value is indicated by a solid circle in figure 1. An alternative method of calculating—substituting our log K'' value in eq (5)—gives the almost identical value 4.35.

The σ value for the group m-$N(CH_3)_2$, derived from published data for the reaction of phenolate ions with propylene oxide in 98 percent ethanol at 70.4°, is -0.211 [31 (d)], and the pK value calculated using this is 4.41. This pK value was used as described in the preceding paragraph for locating a solid circle. Once more, the solid circle falls close to our standard line. The pK value calculated by substituting our log K'' value in eq (5) is 4.37.

One can easily see why it is unsatisfactory to use aqueous ionization constants in assessing the effect of an amino or substituted amino group on the dissociation of the —COOH proton. For one thing, the aminobenzoic acids have *two* ionization constants, and these constants are not very widely separated.[31] Also, the inductive and field effects of the amino group and its resonance with the benzene ring are undoubtedly affected by coordination with water molecules. Furthermore, it has been concluded on the basis of several types of physical evidence that m-aminobenzoic acid exists primarily as the zwitterion in water [34].[32]

An attempt has been made to deduce the effect of the m-NH_2 group on the aqueous ionization of benzoic acid by employing the relationship [34]:

$$pK_D = pK_1 + pK_2 - pK_E. \qquad (8)$$

In eq (8) pK_1 and pK_2 are the experimentally obtained values for the ionization of $H_3\overset{+}{N}$— and —COOH, respectively, pK_E is an experimental value for the ionization of $H_3\overset{+}{N}C_6H_4COOCH_3$ or $H_3\overset{+}{N}C_6H_4COOC_2H_5$ (taken as 3.56 for the m-amino substituted ester), and the value of pK_D is considered to indicate the effect of an *uncharged* m-amino group on the ionic dissociation of the —COOH group. It is assumed that —COOH and —COOR have identical effects on the dissociation of $H_3\overset{+}{N}$—.[33] Using the data of footnote 31 (a) to calculate pK_D gives the value 4.26. This is fairly close to the value

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[29] Bromophthalein magenta E is too insoluble in water for an exact measurement of its pK value, but a rough measurement has indicated this to be, as expected, practically the same as the pK value for bromophenol blue (4.15).

[30] Equation (5) is equivalent to:

$$\log K'' = -2.17\, pK + 14.37; \qquad (7)$$

ρ is the negative coefficient of pK in eq (7).

[31] The following values were obtained in recent attempts to evaluate the thermodynamic pK_1 and pK_2 values for three aminobenzoic acids: (a) For o-, m-, and p-aminobenzoic acids, respectively, pK_1 values obtained by potentiometric procedures are 2.05, 3.07, and 2.38; the corresponding pK_2 values are 4.95, 4.75, and 4.89. (See table 1, footnote j.) (b) For o- and p-aminobenzoic acids, the respective pK_1 values obtained employing spectrophotometry are 2.14 and 2.29, and the pK_2 values, 4.80 and 4.86 [33].

[32] In contrast, the isomeric o and p-substituted acids are thought to exist largely, though not exclusively, as uncharged molecules in water [34].

[33] See [34 (a), ch. 4] for further discussion of this calculation.

(4.35) calculated from our eq (5) and log K'' data. The latter value is probably the more accurate index of the effect of m-NH_2 on the ionization of benzoic acid.

Previously, in the study of reactions in ethanol-water mixtures of varying ethanol content, the substituent constant σ for m-OH has been observed to be very sensitive to the composition of the solvent.[34] An average value, -0.002 [32], was substituted in Hammett's equation in computing the pK value used to locate the solid circle in figure 1. A σ value of about $+0.05$ for m-OH and m-OCH_3 (actually, $+0.04$ and $+0.06$, respectively) is deduced with the use of our eq (5) and log K'' values. Modification of the electrical influences of the two groups resulting from coordination with solvent molecules offers a reasonable explanation of the variation of σ with solvent composition. As with m-NH_2 and m-$N(CH_3)_2$, one may presume the results obtained for benzene solutions to furnish a more reliable index of electrical effects of these substituent groups on the —COOH group than those obtained for aqueous or alcoholic solutions.

In short, it seems correct to conclude that among the *meta*-substituted benzoic acids departures from a linear relation of strengths in water and benzene will be rare, and that explanations for such departures should usually be sought in phenomena characteristic of aqueous systems.

c. *para*-Substituted Benzoic Acids

In analyzing the relative acidic behavior of *para*- and *ortho*-substituted benzoic acids in the solvents benzene and water it is immediately evident that most of the ones studied fail to conform to the "norm" defined in 4.2.b and indicated by the heavy line in figure 2.

For the *para*-substituted acids the departures from the norm are in general rather small.[35] However, it seems apparent that while the acids containing —Cl, —Br, or —I deviate only very slightly from the norm, the acids containing substituents commonly regarded as being decidedly electron-releasing (—F, —OH, —OCH_3, —NH_2) are relatively stronger in benzene than in water whereas the two acids with electron-attracting substituents (—CN, —NO_2) are relatively weaker in benzene than in water. Using data for the seven *para*-substituted acids marked with asterisks in table 1 gives the equation

$$pK = -0.557 \log K'' + 7.218 \qquad (9)$$

as an expression of the relation of the strengths of this group of acids in benzene and water. The straight line corresponding to this equation is indicated by the faint line intersecting the norm in figure 2.

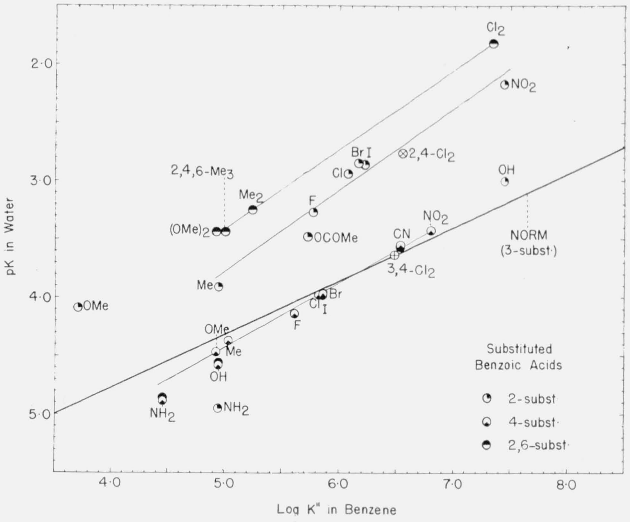

FIGURE 2. *Comparison of the strengths of some 2-, 4-, and 2,6-substituted benzoic acids in benzene and water, as measured by log K'' and pK, respectively; $t=25°$ C.*

The solid circles apply to cases where pK values were calculated using Hammett σ values. In all other cases the values plotted were obtained experimentally.

No attempt will be made here to account in detail for the deviations from linearity, but it is easily seen that bonding of water to a *para* —CN or —NO_2 group (see formula IV) might accentuate the acid-strengthening resonance of either group with the ring. Hydration of —F, —OH, —OCH_3, or —NH_2 could reduce their acid-weakening resonance with the ring (compare formula III); however, the acid-strengthening field effect would also be reduced. As a matter of fact, several investigators have called attention to the existence of a solvent influence on the σ values of *para* substituents like —OH, —$N(CH_3)_2$, —CN, and —NO_2 [32]. The electrical effect of p-CH_3, also, appears to vary somewhat with the medium [35]. For example, values of σ for p—CH_3 ranging from -0.17 (in water) to -0.08 (in hexane) have been calculated from studies of reactions of p-toluidine [35]. It is worth noting that the pK value (4.28) calculated by substituting -0.08 in eq (6) is practically the same as the pK value (4.30) calculated using eq (5) and the log K'' value for p-toluic acid.

It seems evident that the aqueous pK values of *para*-substituted benzoic acids are not infallible indexes of intrinsic acidic strengths or sources of universally valid σ values. In spite of experimental uncertainties in this work, the log K'' values obtained with the benzene solutions are probably, on the whole, more accurate indexes of the relative intrinsic acidities than are the aqueous pK values.

d. Mono-*ortho* and Di-*ortho* Substituted Benzoic Acids

It is well known that the influence of substituents in close proximity to a reacting group, such as the —COOH group of benzoic acid, is generally unpredictable. Reference to some of the recognized anomalies in the strengths of *ortho*-substituted benzoic acids in water, and to some of the attempts

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[34] See p. 232–3 of [32]. In the ionization of m-hydroxybenzoic acid, for example, the value of σ changed from $+0.124$ in water to -0.134 in 100-percent ethanol.

[35] The three solid circles (for p-NH_2, p-OH, and p-CN) that are partly visible in figure 2 have the same significance as in figure 1. That is, they mark the points obtained on plotting against log K'' the pK values *calculated* by using eq (6) with the Hammett σ values given in table 7 of [32]. All three solid circles are slightly closer to our norm than are the corresponding open circles.

to account for the anomalies, was made earlier in this paper (section 4.2.a.). An analysis of the nature and the extent of the deviations of *ortho*-substituted acids from the norm, which has been found to describe the parallelism between the strengths of *meta*-substituted acids in water and in benzene, should be helpful in accounting for part of the anomalies.

On only a casual inspection of figure 2 it is evident that all of the points for *ortho*-substituted acids except one (that for *o*-aminobenzoic acid) are located above the line representing the norm. This means that the acids are either too strong in water or too weak in benzene (or both) for conformance.

The points in question are rather scattered. Using the data for the six acids containing a single halogen, methyl, or nitro group in the *ortho* position the equation

$$pK = -0.70 \log K'' + 7.26 \qquad (10)$$

was calculated by the least squares method. The corresponding line is indicated faintly in figure 2. This line is helpful in guiding the eye to the vicinity of most of the points for mono-*ortho*-substituted acids, but we believe it to represent no more than a crude approximation of a norm for this class of acids.

o-Methoxybenzoic acid is by far the weakest in benzene of all the acids studied. In fact, this acid is so much weaker than bromophthalein magenta E in benzene that the precision of the measurements was very poor (see table 2) and the log K'' value reported is considered only a rough approximation. It can scarcely be doubted that the comparatively feeble tendency for this acid to combine with diphenylguanidine in benzene results from the stability of a chelate structure in which the —COOH proton is attracted toward the oxygen of —OCH_3. Infrared data have already been interpreted as indicating the existence of this structure in another inert solvent, carbon tetrachloride (see footnote 19). In water, hydrogen bonding of the solvent to —OCH_3 would oppose formation of the chelate structure and would also undoubtedly modify the inductive and field effects of —OCH_3 on —COOH and alter its resonance with the benzene ring. Hydration could also increase the bulk of —OCH_3 to such a degree as to cause steric inhibition of resonance of —COOH with the ring.

The point for salicylic (*o*-hydroxybenzoic) acid is so close to the norm as to suggest that in benzene the anion exists largely in the same chelated structure that accounts well for the relatively great acidity of the compound in water—a structure in which the phenolic hydrogen is bonded to a carboxylate oxygen (see section 4.2.a (4)). Possibly the slightly reduced acidity in benzene indicates part of the molecules to be in a chelated form analogous to that which has been suggested for *o*-methoxybenzoic acid. The aqueous *pK* value at 25° for aspirin (*o*-acetylsalicylic acid) has not been measured with the same degree of care as that of many of the other benzoic acids. The value cited, if assumed to be substantially correct, suggests some tendency in inert solvents for chelation of the same type as that of *o*-methoxybenzoic acid.

The case of anthranilic (*o*-aminobenzoic) acid seems too complex for analysis at this time of its differing acidic behavior in benzene and water. Gordy concluded from infrared data [36] that in carbon tetrachloride solutions the amino hydrogen of methyl anthranilate—like the hydroxyl hydrogen of methyl salicylate—is bonded to the carbonyl oxygen. The hypothesis of a chelated *o*-aminobenzoate ion, analogous in structure to the generally accepted salicylate ion structure, appears reasonable. A zwitterionic structure seems less probable (see footnote 32). Perhaps the unpublished studies of hydrogen bonding referred to in [37] will make the acidic behavior of anthranilic acid more comprehensible.

The acidic behavior observed for *o*-toluic acid in benzene is of exceptional interest. Hitherto, on the basis of aqueous *pK* values, *ortho* substitutions have been believed to increase the strength of benzoic acid—*without exception*—even though the methyl group, being less electron-attractive than hydrogen (see section 4.2.a(1)), would be expected to reduce the acidity of benzoic acid when in the *o*-position as well as when in the *m*- and *p*-positions. Table 1 and figure 2 show that this expectation is fulfilled for benzene solutions. That is, a single *o*-CH_3 substituent does not appear to cause steric inhibition of resonance of the —COOH with the aromatic ring *when in benzene solution*. This suggests that in aqueous solutions the clustering of water molecules about —COOH[36] leads to steric inhibition of resonance of the aromatic ring with —COOH in the case of *o*-toluic acid. If this supposition is correct, then hydration of —COOH must contribute generally to steric inhibition of resonance in *ortho*-substituted benzoic acids when in aqueous solutions, resulting in enhancement of their intrinsic acidities.

It would not be justifiable to conclude merely from the preceding discussion that the behavior of *o*-toluic acid in benzene is completely normal. However, a study of figure 3 indicates that this conclusion is warranted. In this figure, the aqueous *pK* values at 25° reported in the literature for a number of *phenols* substituted by methyl or halogen in various positions of the ring (see table 5) have been plotted against the log K'' values for the *benzoic acids* with the corresponding substitutions.[37] There is good evidence that the aqueous *pK* values for methyl-substituted phenols and also those of methyl-substituted pyridinium cations provide valid evidence as to the electrical influence of the methyl group on the acidity of the parent substance, regardless of the position of substitution.[38] Figure 3 reveals a close linear relationship of the strengths of the phenols in water and the strengths of the correspondingly substituted benzoic acids in benzene not only in all cases of substitution in the *m*- or *p*-positions with halogen or methyl, but also in cases of substitution in the *o*-position with a single methyl group. An analogous linear relation-

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[36] The discussion starting on p. 428 of [38] is of interest in this connection.

[37] The log K'' value (4.74) used for 2,4-dimethylbenzoic acid in figure 3 is from incomplete studies of M. M. Davis and M. Paabo.

[38] For example, see the discussion in [27].

ship of the aqueous pK values for pyridinium ions and the log K'' values for benzoic acids can be demonstrated.[39]

Within the experimental uncertainty of the pK and log K'' values, the influence of two methyl groups in the 2,4- or 3,5-positions of phenol or of benzoic acid is additive, and this is also true for 2,6-dimethylphenol (see tables 1 and 5). On the other hand, it is clear from a study of figure 3 and also of tables 1 and 6 that substitution of —CH_3 in both *ortho* positions of benzoic acid produces anomalously great acidities in both benzene and water. In the case of 2,6-dimethylbenzoic acid, for example, the log K'' value for benzene solutions should be about 4.62—that is, 5.26 minus 2(0.32)—if the polar influences of the two *o*-CH_3 groups were additive. Instead, the introduction of a second *o*-CH_3 restores the log K'' value (5.24) almost to that of benzoic acid. In water, as already noted, a single *o*-CH_3 substitution enhances the acidity of benzoic acid (by 0.29 pK unit). The total increment in acidity (0.95 pK unit) produced by two *o*-CH_3 substitutions in benzoic acid shows that the second *o*-CH_3 has more than twice the acidity-augmenting effect of the first *o*-CH_3.

Jenkins, in considering the ionic dissociation constants for aqueous solutions of the isomeric halo- and nitrobenzoic acids, reached the conclusion [40] [40] that the inductive effect of the substituent is the predominant factor, and that anomalies in the ionizing behavior of the *ortho*-substituted acids are nonexistent. However, this opinion has not been universally shared,[41] and the conclusions reached in this paper about the anomalously great strength of *o*-toluic acid in water seem likely to apply to other cases of *ortho*-substitution, at least to cases in which the substituent is comparable in bulk to —CH_3.[42] Nevertheless, it seems probable that an additional factor—a pronounced tendency toward internal hydrogen bonding when in benzene solution—is partly responsible for the displacements from the norm of the points for the four *o*-halobenzoic acids, shown in figure 2 [43] (see also footnote 19).

Figure 3 provides further indirect evidence on this point. In examining this figure no doubt the reader has already noticed the displaced positions of the points for acids substituted in the 2-position with —Br or —Cl. The displacements indicate two possibilities—either there is some factor causing excessively great acidity of the *o*-halophenols in water, or there is a factor reducing the acidity of the *o*-halobenzoic acids in benzene. There is no reason to consider that *o*-halophenols are anomalously strong

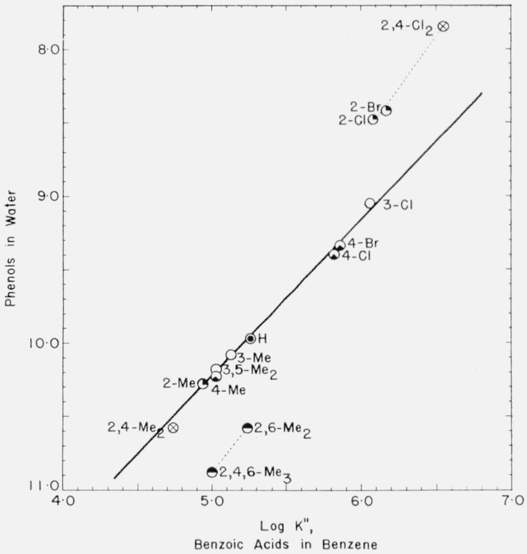

FIGURE 3. *Comparison of the effects of different substitutions on the acidity of phenol in water (as measured by pK) and the acidity of benzoic acid in benzene (as measured by log K''); $t=25°$ C.*

TABLE 5. *Ionic dissociation constants of phenols in water at 25° C*

Substituent [a]	pK	Avg. pK
None*	^{b} 10.00 ^{c} 9.98 ^{d} 9.95 ^{f} 9.94 ^{g} 9.99	9.97
2-Methyl*	^{b} 10.29 ^{f} 10.28	10.28
3-Methyl*	^{b} 10.09 ^{c} 10.08	10.08
4-Methyl*	^{b} 10.26 ^{c} 10.25 ^{f} 10.19	10.23
2,4-Dimethyl	^{f} 10.58	10.58
2,6-Dimethyl	^{g} 10.58	10.58
3,5-Dimethyl*	^{e} 10.17 ^{g} 10.18	10.18
2,4,6-Trimethyl	^{f} 10.88	10.88
2-Bromo	^{d} 8.42	8.42
4-Bromo*	^{c} 9.34	9.34
2-Chloro	^{d} 8.48	8.48
3-Chloro*	^{c} 9.08 ^{d} 9.02	9.05
4-Chloro*	^{c} 9.42 ^{d} 9.38	9.40
2,4-Dichloro	^{d} 7.85	7.85

[a] Asterisks indicate the acids whose pK and log K'' data were used in calculating the equation for the line in figure 3.
[b] A. I. Biggs, Trans. Faraday Soc. **52,** 35 (1956).
[c] F. G. Bordwell and G. D. Cooper, J. Am. Chem. Soc. **74,** 1058 (1952).
[d] C. M. Judson and M. Kilpatrick, J. Am. Chem. Soc. **71,** 3110 (1949).
[e] H. Kloosterziel and H. J. Backer, Rec. trav. chim. **72,** 185 (1953).
[f] G. R. Sprengling and C. W. Lewis, J. Am. Chem. Soc. **73,** 5709 (1953).
[g] G. W. Wheland, R. M. Brownell, and E. C. Mayo, J. Am. Chem. Soc. **70,** 2492 (1948).

TABLE 6. *Calculated and observed increments in the strength of benzoic acid produced by 2, 6-disubstitutions* [a]

2- and 6-substituents	Δ log K'' (benzene)		−Δ pK (water)	
	Calculated	Observed	Calculated	Observed
CH_3	−0.64	−0.02	+0.58	+0.95
Cl	+1.64	+2.08	+2.52	+2.38
OCH_3	−3.2	−0.34	+0.22	+0.76

[a] Data all refer to 25° C, and were computed from the pK and log K'' data given in table 1 for the corresponding mono-*ortho*-substituted acids. Positive and negative increments indicate, respectively, increases and decreases in acidic strength.

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[39] Other evidence bearing on this discussion was obtained by Norris and Strain [39], who compared the rates of reaction of different acids with di-*p*-tolyldiazomethane in toluene at 25° C with the corresponding aqueous ionization constants. They remarked that —Cl, —Br, and —NO_2 in the *o*-position of benzoic acid greatly increase both reactivity and ionization, while —CH_3 and —OCH_3 in the *o*-position increase ionization but decrease reactivity.

[40] See also the discussion in sections IV–G and V of [24 (a)].

[41] For example, see [27, p. 605].

[42] Pauling gives the following tabulation of van der Waals radii (in A) for substituents of interest in this discussion: H, 1.2; F, 1.35; Cl, 1.80; Br, 1.95; I, 2.15; CH_3, 2.0 [41].

[43] An important study of the OH-vibration frequencies of carboxylic acids and phenols, including many *m*- and *p*-substituted benzoic acids, in dilute carbon tetrachloride solutions at 25° C deliberately excluded the compounds *expected* to have internal H-bonds, such as *o*-substituted phenols and benzoic acids [42], but no experimental evidence of hydrogen-bonding in *o*-halobenzoic acids was located in the literature.

in water. Indeed, while Jenkins has concluded that *ortho* effects are absent [43], slightly reduced acidity resulting from persistence of the chelate structure [44] in water has been tentatively deduced from the comparative aqueous pK_a values of substituted phenols and pyridines [45]. Knowledge as to whether the electrical influences of two *o*-halogen substitutions on the aqueous pK value of phenol are additive would be helpful in deciding this question, but the only pK values found in the literature for phenols substituted by halogen in the 2- and 6-positions are untrustworthy. Regardless of which view is correct, the displacement of the points in figure 3 suggests a marked tendency for intramolecular hydrogen bonding of the *o*-halobenzoic acids when in benzene.

o-Nitrobenzoic acid is considered to exhibit only a slight tendency toward chelation, and this is not regarded as surprising, because the chelate ring would be seven-membered [46].

Figure 2 discloses an exact inverse parallelism of the aqueous pK and the log K'' values for the only 2,6-disubstituted acids of suitable strength that were available for inclusion in this study—namely, 2,6-dimethoxy-, 2,6-dimethyl-, 2,6-dichloro-, and 2,4,6-trimethylbenzoic acids.[44] The closely linear relation of the two sets of values may be accidental, and it is clearly desirable to extend pK and log K'' measurements to benzoic acids with other substitutions in the 2- and 6-positions. With two substitutions in the *ortho* position, steric inhibition of resonance appears to result both in water and benzene, whatever the nature of the substituent. But, as table 6 shows, the observed acidities in the two solvents are in marked disagreement with predictions based on the assumption that substitution in both *ortho* positions will produce twice the effect of a single *ortho* substitution.

4.3. Comparative Strengths in Benzene and Other Nonaqueous Solvents

Numerous investigators have studied the effects of different nonaqueous solvents (most commonly, lower alcohols or alcohol-water mixtures) on the relative strengths of acids, employing a variety of experimental procedures—colorimetric, conductometric, kinetic, and potentiometric. A series of systematic studies by Kilpatrick and co-workers is of particular interest for comparison with the results presented in this paper. Some of their results were obtained colorimetrically, but in the most complete set of measurements the strengths of some 20 monosubstituted benzoic acids relative to benzoic acid itself were compared by an emf method in 8 different solvents, 5 of which were anhydrous alcohols and the remaining 3, dioxane-water mixtures of varying dielectric constant [47 and 6]. The method adopted (compare [48]) employed concentration cells of the type:

Au	HB___0. 005 M LiB___0. 005 M LiCl_ 0. 045 M Quinhydrone	LiCl 1. 00 M	HX__ 0. 005 M LiX__ 0. 005 M LiCl_ 0. 045 M Quinhydrone	Au

HB signifies benzoic acid and LiB, its lithium salt; HX signifies the substituted benzoic acid and LiX, its lithium salt. The presence of a high concentration of lithium chloride ensured negligible junction potentials. The equilibrium being measured can be expressed as

$$A_x+B_o^-\rightleftarrows A_o+B_x^- \tag{12}$$

Here, following Brönsted symbolism, A_o and A_x represent benzoic acid and the substituted benzoic acid, respectively, while B_o^- and B_x^- represent the corresponding anions ("conjugate bases"). Using the concentration cell described above, the equilibrium constant at 25° C—referred to as $K_{A_xB_o}$ [47]—can be obtained from the relationship:

$$E(\text{emf})=0.05915 \log K_{A_xB_o}. \tag{13}$$

In cases in which tests were made, the values of $K_{A_xB_o}$ seemed to be independent of the ionic strength [47]. It is evident that log $K_{A_xB_o}$ is equivalent in meaning to such other notations as log K_r [49], log (K_{HB}/K_{HX}), Δ log K, or $-\Delta pK$.[45]

In table 7 the Δ log K values for some 20 *o*-, *m*-, and *p*-substituted benzoic acids in water, in the eight nonaqueous solvents just referred to, and in benzene have been compiled. The values given in table 7 were used in preparing figures 4 to 6, in which the increments $-\Delta pK$ (for aqueous solutions) or the increments log $K_{A_xB_o}$ have been plotted against the increments Δ log K'' obtained in this investigation for benzene solutions.

The symbols used in figures 4 to 6 have the same significance as in figure 2.[46] Also, just as in the preceding figures, each solid line indicates a "norm"—that is, a linear relationship of the strengths of *meta*-substituted benzoic acids in benzene and in the second medium, having the form

$$-\Delta pK(\text{or } \log K_{A_xB_o})=m(\Delta \log K'')+b. \tag{14}$$

The constants m and b of eq (14) for the different media, computed by the least-squares method with the data indicated in table 7, are compiled in table 8. The compilation includes the results for *o*- as well as for *m*-substituted acids.

a. *meta*-Substituted Acids

Taking a "bird's-eye view" of figures 4 to 6 and also referring to the values listed in table 8, it is quickly apparent that for the *meta*-substituted acids the slope increases sharply upon changing from water

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[44] The line connecting the points corresponds to the equation

$$pK=-0.680 \log K''+6.814. \tag{11}$$

The constants of this equation were calculated by the least-squares procedure, using all of the available data.

[45] For our purposes Δlog K values and absolute values of ionic dissociation constants in the various media are equally good. To obtain the latter, a reliable value of the dissociation constant of any one of the series—say, benzoic acid itself—is necessary (see the discussion in [47].

[46] To avoid confusion, only points meriting special attention have been labeled in figures 4 to 6. The remaining points can be identified by the aid of table 7.

TABLE 7. *Effect of the solvent on the comparative strengths of benzoic acid and various of its monosubstituted derivatives at 25° C*

Substituent	$-\Delta pK$[a]	Log $K_{A_xB_o}$ (μ=0.05)[b]								Δlog K''[c]
	Solvent[d]									
	Water	MeOH	EtOH	*n*-PrOH	*n*-BuOH	Ethylene glycol	Dioxane-water, Wt % dioxane			Benzene
							26.5	43.5	73.5	
	(78.5)	(31.5)	(24.2)	(20.1)	(17.4)	(37.6)	(55)	(40)	(15)	(2.28)
	Ortho-substituted benzoic acids									
Br[e]	1.35	1.27	1.16	1.16	1.09	1.20	1.13	1.00	0.88	0.91
Cl[e]	1.26	1.21	1.12	1.09	1.08	1.14	1.08	0.97	.84	.82
F	0.93	1.00	1.02	0.96	0.93	0.69	--------	--------	--------	.51
OH	1.20	1.49	1.63	1.57	1.50	1.50	1.49	1.60	1.78	2.19
I[e]	1.34	1.19	1.08	1.10	1.04	1.10	1.00	0.87	0.75	0.96
OCH_3	0.11	0.17	0.24	0.26	0.28	0.18	−0.06	−.10	−.07	−1.6
CH_3[e]	.29	.09	.02	.04	.00	.05	.04	−.08	−.21	−0.32
NO_2[e]	2.03	1.83	1.77	1.80	1.78	1.74	1.78	1.66	1.58	2.18
	Meta-substituted benzoic acids									
Br[f]	0.39	0.60	0.65	0.63	0.58	0.54	0.43	0.47	0.53	0.80
Cl[f]	.37	.59	.63	.61	.58	.52	.44	.48	.53	.80
F[f]	.34	.51	.53	.52	.42	.45	.41	.41	.49	.68
OH	.12	−.11	−.16	−.16	−.16	−.03	.01	.00	−.02	.09
I[f]	.35	.55	.62	.62	.57	.49	.37	.40	.46	.79
CH_3[f]	−.07	−.09	−.06	−.10	−.10	−.09	−.12	−.14	−.14	−.13
NO_2[f]	.71	1.05	1.17	1.15	1.10	.93	.89	.97	1.06	1.56
CN	.52	0.83	0.97	--------	--------	.73	--------	--------	--------	1.30
	Para-substituted benzoic acids									
Br	0.23	0.42	0.47	0.43	0.42	0.37	--------	0.38	0.43	0.60
Cl	.22	.34	.42	.39	.39	.30	--------	.38	.39	.56
F	.06	.18	.23	.21	.22	.17	0.15	.22	.25	.35
OH	−.38	−.53	−.55	−.57	−.57	−.45	−.42	−.47	−.53	−.32
I	.22	.39	.45	.45	.40	.36	--------	.38	.38	.59
OCH_3	−.27	−.36	−.32	−.36	−.36	−.32	−.33	−.32	−.36	−.34
CH_3	−.17	−.18	−.18	−.21	−.19	−.17	−.23	−.22	−.21	−.23
NO_2	.78	1.02	1.17	1.14	1.14	.96	.97	1.10	1.18	1.54
CN	.65	0.91	1.00	--------	--------	.82	--------	--------	--------	1.27

[a] pK, as usual, equals $-\log K_{\text{dissocn.}}$ $\Delta pK = pK'' - pK''_0$, where K''_0 is the ionization constant of benzoic acid and K'' is the ionization constant of the monosubstituted benzoic acid under consideration. The data given in table 1 were used in computing ΔpK.

[b] Log $K_{A_xB_o}$ is the same as log K''−log K''_0. These values are from the work of Kilpatrick and co-workers [47,6], and were obtained by an emf method. The ionic strength, μ, was mostly due to added lithium chloride. The original results have been rounded off to two decimal places.

[c] $\Delta \log K'' = \log K'' - \log K''_0$; this work, computed from data presented in table 1. As previously emphasized, here K'' and K''_0 are *association* constants.

[d] The dielectric constants of solvents, as stated in the original articles, are given in parentheses below the names.

[e] Indicates the acids the data for which were used in calculating equations pertaining to *ortho*-substituted acids (see table 8).

[f] Indicates the acids the data for which were used in calculating least-squares equations for the solid lines shown in figures 4 to 6. See table 8.

TABLE 8. *Slopes and intercepts of equation (14)*[a]

Solvent	Dielectric Constant	*meta*-Substituent		*ortho*-Substituent	
		Slope	Intercept	Slope	Intercept
Water	78.5	0.461	0	0.742	0.561
Methanol	31.5	.676	0.028	.690	.490
Ethanol	24.2	.730	.043	.694	.399
n-Propanol	20.1	.742	.015	.708	.394
n-Butanol	17.4	.715	−.011	.706	.355
Ethylene glycol	37.6	.606	.019	.670	.436
Dioxane-water	55	.594	−.042	.690	.378
Dioxane-water	40	.654	−.059	.690	.256
Dioxane-water	15	.707	−.042	.710	.122

[a] Equation 14 is $-\Delta pK$ (or log $K_{A_xB_o}$)=m(Δlog K'')+b. See further discussion in the text.

to methanol as a solvent. Moreover, further increases in slope occur on shifting successively to ethanol and *n*-propanol. Such results are to be expected, for as others have pointed out [48,50],[47] an equation of the form

$$\Delta W = e\mu\cos\theta/\epsilon r^2 \tag{15}$$

expresses the increase in the work of ionic dissociation of an acid like benzoic acid upon the introduction of a polar substituent having only an electrostatic effect on the ionizing group. In eq (15) e is the charge on the ion; r is the distance from the substituent to the —COOH group; $\mu\cos\theta$ is the component of the electric moment of the substituent along r; and ϵ is the dielectric constant of the medium. ΔW is negative or positive in sign according as the substituent facilitates or makes more difficult the removal of the proton. The equation, as applied to *meta*-substituted benzoic acids, predicts that changing the solvent to one of lower dielectric constant should cause an increase in the strength relative to benzoic acid when the substituent is one that promotes ionization (for example, —Cl or —NO_2), but a decrease in strength relative to benzoic acid when a substituent such as —CH_3 is present in the ring.

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[47] Also see [47,51].

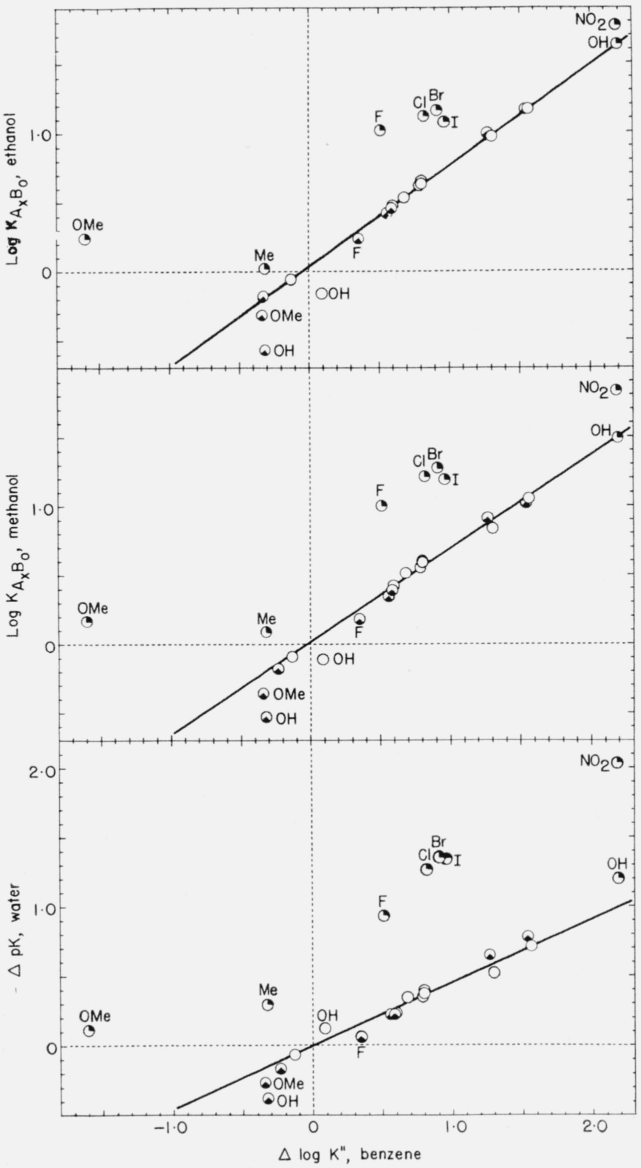

FIGURE 4. *Comparison of the effects of different o-, m-, and p-substitutions on the strength of benzoic acid in benzene, water, methanol, and ethanol at 25° C.*

See table 7 for data used. The symbols have the same significance as in figures 1 and 2.

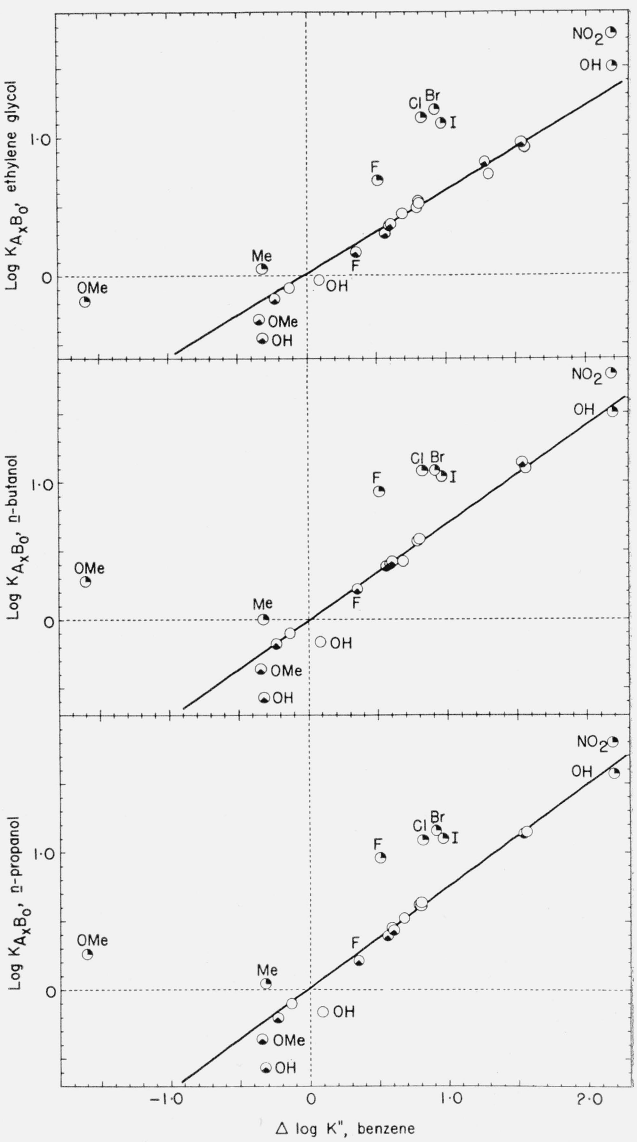

FIGURE 5. *Comparison of the effects of different o-, m-, and p-substitutions on the strength of benzoic acid in benzene, n-propanol, n-butanol, and ethylene glycol at 25° C.*

See table 7 for data used. The symbols have the same significance as in figures 1 and 2.

With the exception of *m*-hydroxybenzoic acid, figures 4 to 6 show close linearity of the strengths of *meta*-substituted acids in benzene and in the other solvents considered here. The existence of solvent effects on the acidic behavior of *m*-hydroxybenzoic acid was previously referred to (see footnote 34). Such effects are also noticeable in table 7 and figures 4 to 6. Thus, while *m*-hydroxybenzoic acid is stronger than benzoic acid in water, as well as in benzene, it appears to be decidedly weaker in all of the monohydric alcohols. On the other hand, the results for ethylene glycol or dioxane-water solutions indicate a strength differing very little from that of benzoic acid. A difference in the manner of hydrogen-bonding of the solvent to the substituent —OH group is possibly a factor in the differing solvent effects on the acidity. Such possibilities would include bonding of the two types:

$$(1)\ \mathrm{HOOC{\cdot}C_6H_4{\cdot}OH\ .\ .\ .\ OH_2}\ \text{and}$$
$$(2)\ \mathrm{HOOC{\cdot}C_6H_4{\cdot}O(.\ .\ .\ HOH)H}$$

The former way, which seems likely to be favored because of the acidic character of a phenolic —OH, should increase the negative charge on the phenolic oxygen. Under such conditions, an enhancement of the acid-strengthening influence of *m*-OH could be expected. With hydrogen-bonding of type (2), however, a reduction of the acid-strengthening influence of *m*-OH could be looked for. In dioxane-water mixtures, perhaps extensive hydrogen-bond-

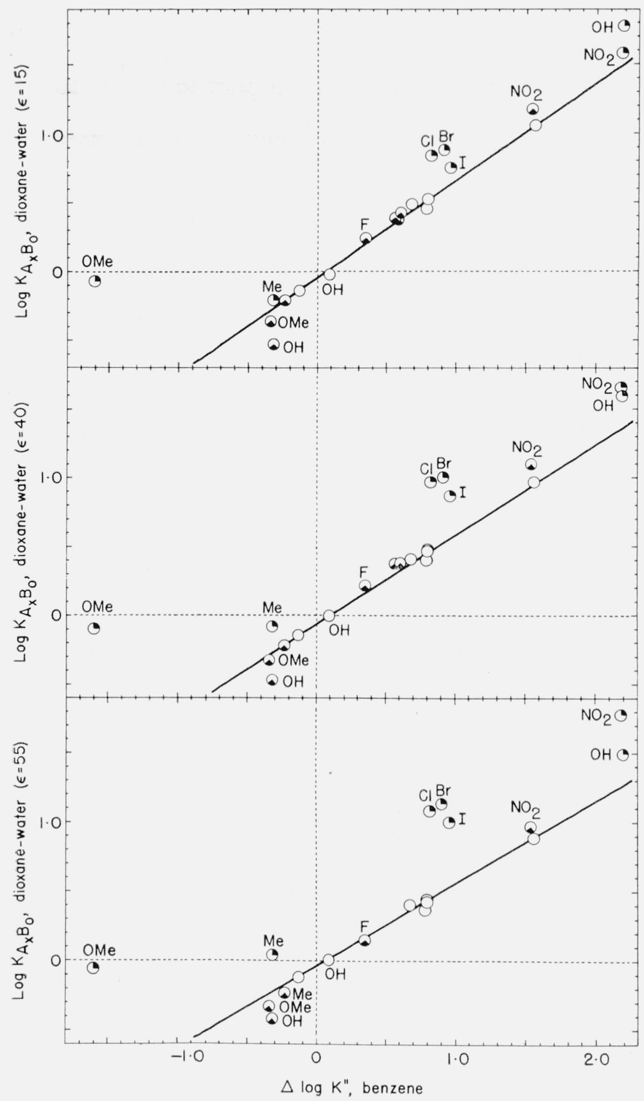

FIGURE 6. *Comparison of the effects of different o-, m-, and p-substitutions on the strength of benzoic acid in benzene and in three dioxane-water mixtures having the dielectric constants 55, 40, and 15, respectively; t=25° C.*

See table 7 for data used. The symbols have the same significance as in figures 1 and 2.

ing of dioxane with water [52] appreciably reduces solvation of the *m*-OH group.

b. *para*-Substituted Acids

Most of the *para*-substituted acids conform well to the norms indicated in figures 4 to 6. However, *p*-hydroxybenzoic acid is seen to be decidedly weaker in all of the alcohols and dioxane-water mixtures than in benzene. *p*-Methoxybenzoic acid shows the same weakening, but to a smaller degree. Hydrogen-bonding of solvent to the —OH or —OCH_3 group (compare 4.2.b and 4.3.a) offers a reasonable explanation for the reduced strength. A similar tendency for hydrogen-bonding to *p*-F seems indicated for water and all of the alcohols except *n*-butanol (figs. 4 and 5), although it is not evident for dioxane-water mixtures (fig. 6).

The points for *p*-nitrobenzoic acid suggest that its strength is anomalously great in water and in partly aqueous solvents, although not so in the alcohols. This conclusion, if correct, is understandable, as the six-membered ring formed by bonding of both hydrogens of water to the oxygens of the —NO_2 group should have greater stability than structures formed by hydrogen-bonding of alcohol molecules to the —NO_2 group. As mentioned above (section 4.2.c), the expected effect of solvation of the nitro group is enhancement of the acidity.

c. *ortho*-Substituted Acids

A glance at table 8 reveals that the slopes of eq (14), as calculated from data for *ortho*-substituted acids (see table 7), range from 0.69 to 0.71 except in one case—that in which *water* was the solvent being compared with benzene. The approximate constancy in slope contrasts sharply with the variation in slopes (from 0.46 to 0.71), previously noted for *meta*-substituted acids. This variation was shown (4.2.b) to be consistent with the thesis that the influence of *m*-substituents on the acidity of benzoic acid is principally electrostatic in nature. The near constancy of slope for *o*-substituted acids, irrespective of the dielectric constant of the solvent, indicates that the influence of *o*-substituents on —COOH is not solely an electrostatic effect. Instead, we must conclude—as so many others have done in studying effects of *ortho*-substitutions on various benzene side-chain reactions—that local effects such as steric hindrance and hydrogen-bonding are very important.

Figures 4 and 5 show that deviations of *o*-substituted acids from the norm are smaller in the case of alcohols than in the case of water. Furthermore, the general picture is much the same for all of the alcohols. However, increasing the dioxane content of dioxane-water mixtures (see fig. 6) has the effect of bringing the points for most of the *o*-substituted acids closer to the norm until in the dioxane-water solvent of lowest dielectric constant (15), the only major remaining deviation is in the case of *o*-methoxybenzoic acid. The chelation of *o*-methoxybenzoic acid obviously does not persist in solvents which, like the alcohols or dioxane-water, can become hydrogen-bonded to the —OCH_3 group.

Previously, in comparing relative strengths in benzene and water (see 4.2.d and fig. 2), the small displacement from the norm of the point for salicylic acid was assumed to indicate a reduced strength in benzene, and it was suggested that in benzene part of the acid may have a chelated structure analogous to that of *o*-methoxybenzoic acid. However, the points for salicylic acid are not displaced from the norms in the plots for the four monohydric alcohols (figs. 4 and 5). Therefore, an alternative explanation—hydrogen-bonding of solvent molecules to the *o*-OH group—should not be excluded in accounting for the departures from the norms observed for solutions in water, dioxane-water, and ethylene glycol.[48]

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[48] This alternative explanation is in harmony with the suggestion (see p. 480 of [47(a)]) that the acid-strengthening type of chelation becomes favored as the number of hydroxyl groups in the solvent available for solvation of —COOH decreases (which occurs in alcohols as the dielectric constant decreases).

It seems desirable to reemphasize what we consider an especially important result of this investigation: the discovery that *o*-toluic acid shows normal acidity in benzene, instead of the anomalously high acidity exhibited when in aqueous solutions (4.2.d). This must mean that steric inhibition of resonance when in water—which seems the most reasonable of the explanations that have been offered for the enhanced acidity of this acid—results because solvent molecules become attached to the —COOH group. From figures 4 to 6 one would judge that solvation is most marked in water solutions. Evidently it falls off as increasing amounts of the water are replaced by dioxane, as shown by the progressive approach of the points for *o*-toluic acid to the lines representing norms. For the solvent that contained 73.5 weight-percent of dioxane ($\epsilon=15$) the point is very close to the norm.[49] In the alcohols the acidity of *o*-toluic acid appears to be much less enhanced by solvation of the —COOH group.[50]

To reiterate what was said above (4.2.d), the findings about *o*-toluic acid make it seem probable that hydration of the —COOH contributes rather generally to enhancement of the strengths of *ortho*-substituted benzoic acids when in water-containing solvents, because the added bulk promotes steric inhibition of resonance. In alcoholic solutions, also, solvation probably produces some steric inhibition of resonance, with consequent enhancement of acidity, but solvation by alcohols seems less prone to occur than solvation by water.

Our previous conclusion (4.2.d) that the reactivities of *o*-halobenzoic acids in benzene are reduced by internal hydrogen-bonding is further supported by the displacements to be noted in figures 4 to 6. Earlier it was suggested [53] that chelation of *o*-halobenzoic acids[51] occurs to an increasing extent with decreasing dielectric constant of the solvent, as in passing successively from water to methanol, then to ethanol. This would imply still greater chelation in benzene. However, a relationship of chelation to the hydrogen-bonding capacity of the solvent seems more probable than a relationship to the dielectric constant. To sum up the discussion of *o*-halobenzoic acids:

(1) Internal hydrogen-bonding (chelation) appears to be an important factor in the reductions in apparent acidity observed on changing from water to nonaqueous solvents such as those dealt with here. This conclusion seems to apply to *o*-fluoro- as well as to the other *o*-halobenzoic acids.

(2) For at least some of the group (those having an *o*-substituent comparable in bulk to —CH_3) steric inhibition of resonance consequent to solvation of the —COOH group may tend to augment the acidity in solvents of good solvating power—water in particular.

As to *o*-nitrobenzoic acid, solvation of the —NO_2 group by the solvent when in water may be of importance (compare 4.3.b), as well as the two factors suggested in accounting for solvent effects on *o*-halobenzoic acid. Here there seems to be somewhat less basis, however, for attributing an important role to chelation.

The literature on the acidic strengths of benzoic acids having the same group substituted in *both ortho*-positions is meager, even for aqueous solutions (compare footnotes o and q of table 1). In reviewing the work of other investigators we have noted only one case of such an acid—that of 2,4,6-trimethylbenzoic acid—in which the effect of a change of solvent (from water to *n*-butanol) on the acidity was measured [48]. Further studies of the sort should be valuable in judging how steric inhibition of resonance, and likewise hydrogen-bonding, affect the strengths of benzoic acids.

This section may be concluded by citing a few important pioneering studies [48, 49, 54] by authors who clearly recognized that changes of solvent may markedly alter relations in the strengths of acids, notably such acids as *o*-substituted benzoic acids. Their observations and conclusions, though more fragmentary, were in general harmony with those which have been presented above.

4.4. Correlations With Other Spectral Data

a. Ultraviolet Data

Of late years there has been a marked growth of interest in the study of steric effects on the electronic spectra of conjugated systems. Included in these studies have been some attempts to correlate ultraviolet absorption spectra of substituted benzoic acids with the nature and position of substituent groups. In one such study, with dioxane as the solvent, it was concluded that steric inhibition of resonance occurs in 2,6-dichlorobenzoic acid, but not appreciably in 2,4-dichlorobenzoic acid [55]. Later, in a more comprehensive study, ultraviolet absorption curves were obtained for benzoic acid itself and the derivatives *o*-, *m*-, and *p*-monosubstituted and 2,6-disubstituted with —CH_3, —Cl, —Br, —OCH_3, or —OH, all in 95-percent ethanol [56]. Still more recently, data have been obtained for absolute ethanol solutions of the benzoic acids substituted in the *o*-, *m*-, and *p*-positions with —F, —I, and —NO_2 [57(a)]. In most cases these acids were found to exhibit three absorption bands in the ultraviolet region, which have been designated as the A, B, and C bands [56]. Of these bands, the B-band (located in the vicinity of 230 mμ) seems most sensitive to steric effects of substituents. The C-band seems to be comparatively insensitive to small steric effects, but sensitive to hydrogen-bonding [56, 57].

The ultraviolet absorption spectra of *meta*-substituted acids show a general resemblance to the spectrum of benzoic acid, but with slightly decreased absorption intensity attributed to inductive effects. The B-band of *para*-substituted acids shows a considerable bathochromic shift from its position in benzoic acid, the extent of the shift paralleling approximately the mesomeric (resonance) effect of the substituent, and the intensity of the B-band

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[49] The marked reduction in the strength of *o*-toluic acid in the two dioxane-water solvents of lowest dielectric constant was noted earlier [47 (d)] (also see [53]). However, no explanation could be offered at that period.

[50] Enhancement of acidity resulting from solvation of the —CH_3 group seems improbable.

[51] And also of *o*-nitrobenzoic acid. Chelation of *o*-fluorobenzoic acid was considered unlikely, however.

also shows marked enhancement; here, the inductive effect seems to be of secondary importance [56, 57].[52]

In the most recent analyses of the effects of steric hindrance on B-bands the following assumptions have been made [57]:

(1) *o*-Disubstituted derivatives (when in neutral solutions) would have approximately the same absorption as that of their *p*-isomers were it not for steric interference with resonance.

(2) Three types of steric effects can be distinguished—(a) Reduced intensity of absorption, produced when steric interference is slight; (b) a shift in the wavelength of absorption, accompanied by reduced intensity, caused by a somewhat greater degree of steric interference; (c) more or less complete disappearance of the B-band,[53] when steric effects are large.

In line with these assumptions, the benzoic acids with a single *ortho*-substituent generally exhibit steric interference of type (b), whereas the effect of di-*ortho*-substitution is of type (c) [55 to 57]. For details the reader is referred to the papers cited.

However, one point merits special attention here: the puzzling spectral behavior of *o*-toluic acid [57 (a)].[54] *o*-Methylacetophenone, where the —OH of *o*-toluic acid is replaced by —CH_3, shows little evidence of steric hindrance to resonance, and it therefore seemed surprising that the alcoholic absorption spectrum of *o*-toluic acid, when compared with that of *p*-toluic acid, exhibits a pronounced hypsochromic shift of the B-band together with marked reduction in the intensity of absorption. To account for this discrepancy the usual explanation of the steric effect due to an *o*-substituent had to be modified [57 (a)]. Now the evidence obtained in this investigation (4.3.c) that steric inhibition of resonance in *o*-toluic acid is evident only when the solvent (water, alcohols) is one which would tend to solvate the —COOH group appears applicable to the problem of interpreting the ultraviolet absorption spectrum of *o*-toluic acid when in alcoholic solution. It seems likely that solvent effects on ultraviolet absorption—which are evident even for benzoic acid [59]—will prove to be still more noticeable for *o*-toluic and other *o*-substituted acids, and that further progress in the correlation of ultraviolet spectra and steric interferences can be accelerated by accumulation of data for solutions in hydrocarbon solvents.

b. Infrared Data

Goulden measured OH-vibration frequencies of 67 carboxylic acids and phenols in dilute carbon tetrachloride solutions at 25° C, to determine whether the frequencies could be correlated with the aqueous *pK* values [42] (see footnote 43). Four correlations of OH-frequencies with *p*H values were discovered—one for the phenols and three for carboxylic acids.

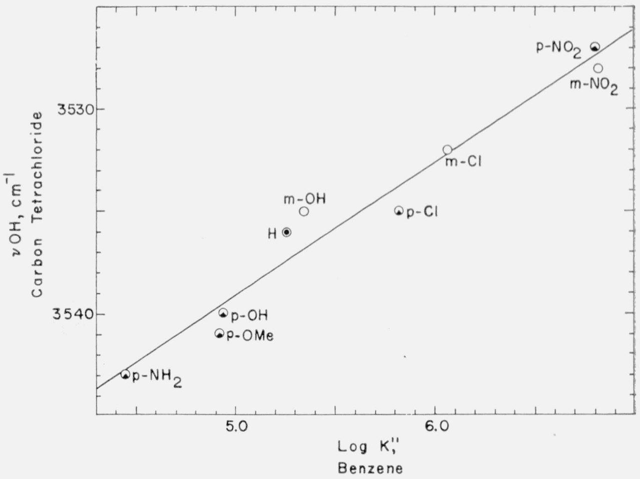

FIGURE 7. *Relationship of* OH-*vibration frequencies of m- and p-substituted benzoic acids when dissolved in carbon tetrachloride and the log K'' values for combination with diphenylguanidine in benzene.* $t=25°$ *C.*

The carboxylic acids were divided into the following types: (1) Those containing $-C=C-COOH$. This included unsaturated aliphatic, naphthoic, cinnamic, and substituted benzoic acids. (2) The $R_3C-COOH$ type, where R=alkyl, halogen, phenoxy, or methoxy. (3) The type $-C=C-CH_2-COOH$.

Nine of the benzoic acids (all *m*- or *p*-substituted) included in Goulden's study were the same as ones included in this study. Figure 7 shows the correlation of the OH-vibration frequencies [55] with the log K'' values obtained in this work. The degree of linearity is excellent considering the experimental uncertainties in both sets of measurements.

Although measurement of the OH-vibration frequencies of *o*-substituted benzoic acids in carbon tetrachloride was not undertaken, because a good correlation with the aqueous *pK* values was not to be expected, it is to be hoped that such infrared data will become available. They should be valuable in accounting for solvent effects on the acidic behavior of *o*-substituted benzoic acids.

Thompson and Steel [60] computed the logarithms of the intensities of the fundamental vibration bands of the —CN group in various *m*- and *p*-substituted benzonitriles, and found good linearity of the values with the Hammett σ values. They suggested that it may be "legitimate" to read off from their plots the σ values corresponding to the band intensities observed for five *ortho*-substituted benzonitriles. In a similar way the Δ log K'' values and the value for ρ (2.17) (see footnote 30), obtained in this investigation can be used to deduce σ values for *ortho* substituents. Table 9 compares the five values deduced by Thompson and Steel with the corresponding values derived from data given in this paper. Both methods of estimating σ give almost the same results for *o*-CH_3, *o*-Cl, and *o*-NO_2. Good agreement in the two sets of values for *o*-NH_2 and

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[52] The spectra of *m*- and *p*-nitro- and iodobenzoic acids are irregular, showing dominating effects of the —NO_2 and —I groups [57(a)].

[53] The absorption bands characteristic of separate chromophoric groups in a molecule disappear when the chromophores become conjugated, being replaced by a "conjugation" band [58], here referred to as the B-band. When the B-band disappears because of steric inhibition of resonance the separate bands are observed.

[54] Also see p. 807 of [56].

[55] These were thought to be accurate to ±1 cm^{-1} for most acids, and ±2 cm^{-1} for the more difficultly soluble ones [42].

TABLE 9. *Hammett sigma values deduced for ortho substituents*

ortho substituent	σ value, ref. 60	σ value, this work
NH_2	−0.35	−0.15
OH	−.2	+1.01
CH_3	−.1	−0.15
Cl	+.4	+.38
NO_2	+.95	+1.00

o-OH is not to be expected in view of the evidence of hydrogen bonding with the —COOH group in anthranilic and salicylic acids. However, on the assumption that the influence of $-NH_2$ or —OH is largely governed by resonance and is about the same in the *ortho* and *para* positions [61], one may estimate σ values for *o*-NH_2 and *o*-OH from the log K'' values for *p*-amino- and *p*-hydroxybenzoic acids. These values (respectively, −0.37 and −0.15) are strikingly similar to the values deduced by Thompson and Steel.

4.5. Summary and Concluding Remarks

Hitherto no method has existed for measuring the relative strengths in benzene of acids comparable in strength to benzoic acid. This paper has described a spectrophotometric method, using 1,3-diphenylguanidine and bromophthalein magenta E as special reagents, for securing such information. The results, which were obtained at 25° C, are expressed as equilibrium constants for association with diphenylguanidine. The acids for which measurements were made were benzoic acid itself, 31 of its monosubstituted derivatives (including all of the acids substituted in the *o*, *m*-, or *p*- positions with $-NH_2$, —Br, —Cl, —F, —OH, —I, $-OCH_3$, $-CH_3$, or $-NO_2$) and eight di- or tri-substituted benzoic acids (including acids with —Cl, $-OCH_3$, or $-CH_3$ in both *ortho*-positions).

The relative strengths of the benzoic acids in benzene have been compared with previously published data (obtained by electrochemical methods) on the relative strengths in water, methanol, ethanol, *n*-propanol, *n*-butanol, ethylene glycol, and three dioxane-water mixtures. In the case of the *meta*-substituted acids, except for *m*-hydroxybenzoic acid, an exact order of relative strengths is preserved in all of the solvents mentioned, supporting previous evidence that the electrostatic effect of the substituent is the dominating influence on the acidity. Irregularities in the behavior of *m*-hydroxybenzoic acid are attributed to hydrogen-bonding with solvent molecules. For *para*-substituted acids, also, a constant relation of strengths is generally preserved in the solvents in question, but here there is evidence that solvation of the substituent sometimes increases and sometimes decreases its influence on the acidity. The relative acidities measured in benzene for these two groups of acids are thought to reflect the intrinsic acidities more accurately than the acidities measured in the other solvents mentioned.

Previous investigators have recognized that a group of acids that includes *ortho*-substituted benzoic acids is likely to show inversions in the order of strengths when the solvent is changed—even when the change is to a solvent of closely similar type (as, for example, in changing from water to a lower alcohol). Comparisons made in this paper of relative strengths in the various solvents have led to several conclusions, prominent among which are the following:

(1) Hydration of the —COOH group appears to enhance the acidic behavior of *ortho*-substituted acids in water. Thus, *o*-toluic acid, which is recognized as being anomalously strong in water, shows normal acidic behavior in benzene. This conclusion has a bearing on attempts to relate apparent acidities with structure or with spectral absorption in the ultraviolet region.

(2) Internal hydrogen-bonding (chelation) markedly depresses the reactivity of *o*-methoxybenzoic acid as an acid when in benzene. The chelated structure has little or no tendency to persist in solvents with hydrogen-bonding capacity.

(3) *o*-Halobenzoic acids appear relatively weaker in benzene than in the other solvents, although the effect is much less marked than with *o*-methoxybenzoic acid. This weakening is probably partly caused by a tendency toward chelation in benzene. Infrared evidence on this question is needed. An enhancement of acidity in water by hydration of the —COOH group also appears probable.

(4) A still smaller tendency toward chelation seems evident for *o*-nitrobenzoic acid. There also appears to be enhancement of the acidity in aqueous solvents. Here, hydration of the $-NO_2$ group seems a probable factor.

(5) The effect of a second *ortho*-substitution on the acidity, as indicated by the available data—which exist only for a few acids, in the solvents water and benzene—is far from additive. Further study of such acids is needed for improved understanding of steric effects on acidity (as well as on spectral absorption).

It seems desirable to underline the conclusion that the acidities measured in water do not provide a completely accurate scale of relative intrinsic strengths. The proton, to be sure, is very minute in size, but one should bear in mind that it does not exist in solutions as an independent entity. Water, because of its great hydrogen-bonding capacity, can not only solvate the proton (with four water molecules per proton, according to the most recent estimate) but also can solvate substituents in the benzoic acid molecule, as well as the —COOH group, with consequent modifications of electrostatic, resonance, and steric effects. The most complete understanding of the relation of structure and acidity can be gained by systematic measurements in solvents of varied types.

Another point to be noted is that information on interactions of colorless acids and bases can be obtained spectrophotometrically by measurements in the visible region, as well as by measurements in the infrared or ultraviolet. The possibility of measurements in the visible region greatly extends the range of solvents that can be used. An indicator dye of suitable characteristics is needed, of course, and a suitable reference base must also be available. Further studies in all of the spectral regions are very desirable.

No reader should be left with the impression that benzoic acids are exceptional in showing inversions in the order of strength on changes of solvent. There is much additional evidence in the literature of solvent effects on relative acidities. For example, the effect of changes of solvent may be different for groups such as cation acids (with some divisions into subgroups), phenols, aliphatic acids, and aromatic acids. One of the most comprehensive reviews on effects of solvents on the strengths of acids was published in a Russian periodical [62]. The existence of such varied solvent effects indicates that no exact, universally valid scale of relative strengths can be constructed. However, in various areas of limited scope acidity scales of practical usefulness should be obtainable. Studies of relative acidities in various solvent media should be helpful in defining such areas.

Finally, the studies reported here, although they represent only the beginning of an effort to gain needed information about acid-base interactions in solvents like benzene, point to a few applications of immediate practical interest. Thus, the solvent effects on acidity which create problems in the construction of practical acidity scales may be turned to advantage in effecting separations and in selecting conditions for obtaining more distinct end-points in titrations of mixtures. A possible application of the method described here is in getting a quick estimate of the acidity of an acid, especially of an acid almost insoluble in water (see 3.2). Such measurements consume only a minute quantity of acid—usually less than a centigram. One more suggested application is in estimating the dimer-monomer equilibrium constants of carboxylic acids in benzene, as illustrated in 4.1. Table 3 illustrates the serious need for such data.

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