

position, in view of the slowness in the attainment of equilibrium, would be very difficult to fix.

An alternative possibility is that the two salts form a single solid solution, theoretically continuous from one pure salt to the other, but that the distribution of the salts between the solid and liquid phases is very uneven. The wide divergence of the tie-lines for complexes giving solutions containing approximately 6% sodium bromate (point B) would then simply indicate a marked tendency toward the formation of an isothermally invariant point, because of a tendency toward discontinuity in the solid phase. The observed curvature at the point B, however, suggests actual discontinuity, so that the latter interpretation, while not impossible, seems rather unlikely.

The solid phases are therefore suggested as being pure sodium bromate from D to C, solid solution of some sodium chlorate in sodium bromate (S.S. I) from C to B, and a solid solution (S.S. II) of wide range of proportions of the salts, up to pure sodium chlorate, from B to A. If this interpretation is correct, this system might then be taken as another example of the type of solid solution formation suggested as possible in connection with a study of the system $\text{NaBrO}_3\text{-Na}_2\text{SO}_4\text{-H}_2\text{O}^2$; that is, a system in which the miscibility of the salts is such that while solid solutions are formed, a pure salt may still constitute one of the solid phases by itself.

The same general characteristics were noted for the system in the results of a partial isotherm at 50° , also shown in Table II.

Summary

1. In the system $\text{KBrO}_3\text{-KClO}_3\text{-H}_2\text{O}$, studied at 25° , the two salts dissolve to a limited extent in each other, forming two solid solutions containing up to 3% potassium chlorate in potassium bromate and up to 5% potassium bromate in potassium chlorate.

2. The salts in the system $\text{NaBrO}_3\text{-NaClO}_3\text{-H}_2\text{O}$ studied at 25° (and incompletely at 50°) form a series of solid solutions which, though the evidence is not altogether conclusive, is apparently discontinuous. The solubility curve at 25° appears to be divided into three portions corresponding to the following solid phases: (1) pure sodium bromate, (2) a sodium bromate solid solution containing up to about 5-10% sodium chlorate, (3) a sodium chlorate solid solution containing from 0 to 60-65% sodium bromate.

3. Conditions for the differential iodometric titration of bromate in the presence of very large amounts of chlorate are examined; with proper correction for the slow reaction of chlorate with iodide in acid solution, small amounts of bromate (0.1-0.2 g.) can be determined accurately in the presence of up to 20 g. of chlorate.

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

The Electrostatic Effect of Substituents on the Dissociation Constants of Organic Acids. IV. Aromatic Acids¹

BY F. H. WESTHEIMER

I

In 1923 Bjerrum² advanced the hypothesis that, except for a statistical factor, the effect of a substituent on the ionization constant of an organic acid is electrostatic in origin. Recently, a more satisfactory mathematical formulation of Bjerrum's hypothesis has been advanced by Kirkwood and the author.³ This treatment differs from the old essentially in that the solute molecules are regarded as cavities of low dielectric constant within the sol-

vent. Shookhoff and the author⁴ have applied the new equations with considerable success to a large number of saturated aliphatic acids, and have shown that it will account not only for the ratio of the first to the second dissociation constants of straight-chain dibasic acids, but also, in contrast to the equations of Bjerrum and of Eucken,⁵ for the ratio of the dissociation constants of alkylated dibasic acids and for the effect of dipolar substituents on the ionization constants of monobasic acids.

The purpose of the present paper is to apply the new treatment to aromatic acids.

(1) Presented on April 5, 1939, at the Baltimore meeting of the American Chemical Society.

(2) Bjerrum, *Z. physik. Chem.*, **106**, 219 (1923).

(3) Kirkwood and Westheimer, *J. Chem. Phys.*, **6**, 506 (1938); Westheimer and Kirkwood, *ibid.*, **6**, 513 (1938).

(4) Westheimer and Shookhoff, *THIS JOURNAL*, **61**, 555 (1939).

(5) Eucken, *Z. angew. Chem.*, **45**, 203 (1932).

The equations from which the effect of substituents on the ionization constants of acids can be computed are given below. For dibasic acids

$$\text{Log } K_1/\sigma K_2 = \frac{e^2}{2.303kTRD_E} = \Delta pK$$

and for dipole substituted acids

$$\text{Log } K_1/\sigma K_2 = \frac{eM \cos \zeta}{2.303kTR^2D_E} = \Delta pK$$

In the first equation K_1 and K_2 are the first and second ionization constants of the dibasic acid, e the electronic charge, and R the distance between the ionizable protons. σ , the statistical factor, is equal to four for the dibasic acids and to two in the comparison of hydroquinone with phenol; in the other cases considered in this paper it is unity. In the second equation, K_1 is the dissociation constant of the acid with a polar substituent, K_2 that of the unsubstituted acid, M the dipole moment of the substituent, ζ the angle the dipole makes with the line joining its center with the ionizable proton, and R the distance between the dipole and the proton. D_E , the "effective" dielectric constant, has been evaluated in the previous papers of this series only for spheres and for prolate ellipsoids of revolution in which the substituent and the dipole are at the foci. While neither a sphere nor a prolate ellipsoid of revolution is a good model for aromatic compounds, the ellipsoid will serve as a first approximation for the para substituted benzene derivatives; obviously neither the ortho nor meta compounds can be treated quantitatively. That meta substituted carboxylic acids are, in general, similar to the para, follows from the work of Dippy and Watson.⁶ The author is aware of the peculiarities of ortho substituted acids,⁷ and hopes to discuss these at a later date.

In the previous publications, the interprotonic or proton-dipole separation has been computed from the known ionization constants, and this length compared with molecular dimensions. In the present instance, it is more advantageous to assume a reasonable distance for the interprotonic or proton-dipole separation, and to compute ΔpK , the difference between the pK values of the two acids (less the logarithm of the statistical factor), a difference which can then be compared with the experimental value. The lengths chosen are, in all cases, reasonable ones. However, variation

(6) Dippy and Watson, *Chem. and Ind.*, **54**, 735 (1935).

(7) Cf. Waters, *Phil. Mag.*, [7] **8**, 436 (1929); Hammett, *J. Chem. Phys.*, **4**, 613 (1936).

of 0.2 Å. will, in the case of the benzoic acids, cause a change of ΔpK of 20%. Since the equation employed is not ideally adapted to benzenoid compounds, and since the lengths chosen for R are somewhat arbitrary, values of ΔpK have been given only to the nearest 0.05 unit. The molecular volumes, necessary for the computations, have been estimated from Traube's rule.⁸ The internal dielectric constant³ has been set equal to 2.00, as in previous papers of this series.

II

The limited data available for dibasic acids are summarized in Table I.

TABLE I

DIBASIC AROMATIC ACIDS		
$V = 190 \text{ \AA}^3$ $R = 7.5 \text{ \AA}$ $D_E = 76$		
Acid	ΔpK (obsd.)	ΔpK (calcd.)
Terephthalic acid ^a	(0.70)	0.40
Benzoic acid <i>p</i> -sulfonamide ^b		
Benzoic acid <i>p</i> -sulfonate	0.35	0.40

^a Due to its insolubility, the first dissociation constant of terephthalic acid has never been measured in water. The estimate in parentheses is that of Kuhn and Wasserman, *Helv. Chim. Acta*, **11**, 44 (1928). ^b The assumption is made that the ionization constant of benzoic acid *p*-sulfonamide is equal to the ionization of the carboxyl group, were it possible to measure it, of benzoic acid *p*-sulfonic acid. The data are given in Landolt-Börnstein, "Physikalisch-chemische Tabellen."

Inspection of this table reveals that the electrostatic effect, while it may not be the exclusive factor, is the major one in determining the effect of a charged group on the strength of an aromatic carboxylic acid.

Since the benzene ring itself introduces complications absent in the aliphatic series, a purely electrostatic treatment will be expected to apply best to the phenylacetic acids, in which a methylene group separates the carboxyl from the ring. The data are collected in Table II. The differences between the dipole moment of the substituents and the hydrogen moment are those given by Smyth⁹ for aromatic compounds, and are assumed to be located in the bond between the ring and the substituent. The calculated value for the *p*-methoxy acid has been placed in parentheses because the angle and location of the methoxyl moment is still in doubt.¹⁰ The calculations have

(8) Traube, *Samml. chem. chem.-tech. Vortr.*, **4**, 255 (1899).

(9) Smyth, *J. Phys. Chem.*, **41**, 209 (1937).

(10) Cowley and Partington, *J. Chem. Soc.*, 1257 (1933); Bennett and Glasstone, *Proc. Roy. Soc. (London)*, **146A**, 71 (1934); Bennett, *Trans. Faraday Soc.*, **30**, 853 (1934); Hampson and Sutton, *Proc. Roy. Soc. (London)*, **140A**, 562 (1933); Sutton and Hampson, *Trans. Faraday Soc.*, **31**, 945 (1935).

been made on the assumption that the value of Marsden and Sutton¹¹ is correct, namely, that the methoxyl moment is at an angle of 76° with the ring to oxygen bond, with the negative end of the dipole toward the ring. While this seems to be the best available estimate, it indicates considerable interaction between the methoxyl group and the ring, causing a complex charge distribution which is poorly represented by a point dipole.

TABLE II

PHENYLACETIC ACIDS			
$V = 210 \text{ \AA.}^3$	$R = 6.6 \text{ \AA.}$	$\cos \zeta = 0.90$	$D_E = 10.9$
Acid	ΔpK (obsd.)	ΔpK (calcd.)	
<i>p</i> -Chlorophenylacetic acid ^a	0.10	0.15	
<i>p</i> -Bromophenylacetic acid ^a	.10	.15	
<i>p</i> -Iodophenylacetic acid ^a	.15	.15	
<i>p</i> -Nitrophenylacetic acid ^a	.45	.40	
<i>p</i> -Methoxyphenylacetic acid ^a	-.05	(-.05)	

^a Dippy and Williams, *J. Chem. Soc.*, 161 (1934); 1888 (1934).

It is apparent that the electrostatic effect alone is adequate to account for the effect of substituents on the ionization constants of phenylacetic acids.

The data for the substituted benzoic acids are summarized in Table III. *p*-Aminobenzoic acid is not included because, since an unknown percentage of the acid is present as a dipolar ion (zwitterion), the value of ΔpK is not known.

TABLE III

BENZOIC ACIDS		
$V = 180 \text{ \AA.}^3$	$R = 5.9 \text{ \AA.}$	$D_E = 9.4$
Acid	ΔpK (obsd.)	ΔpK (calcd.)
<i>p</i> -Toluic acid ^a	-0.15	-0.05
<i>p</i> -Fluorobenzoic acid ^a	.10	.25
<i>p</i> -Chlorobenzoic acid ^a	.25	.25
<i>p</i> -Bromobenzoic acid ^a	.25	.25
<i>p</i> -Cyanobenzoic acid ^b	.70	.70
<i>p</i> -Nitrobenzoic acid ^a	.80	.65
<i>p</i> -Anisic acid ^a	-.30	(-.05)
<i>p</i> -Hydroxybenzoic acid ^b	-.25	(-.00)

^a Dippy and Williams, *J. Chem. Soc.*, 1888 (1934); Dippy, Williams and Lewis, 343 (1935); Dippy and Lewis, 644 (1936). ^b Landolt-Börnstein, "Physikalisch-chemische Tabellen."

Inspection of Table II shows that the electrostatic effect, if not the only one, is at least the major cause of the differences in acidity among the benzoic acids, except for the cases of the hydroxy and methoxy substituted acids.

The close correspondence between the predictions of the electrostatic theory and experiment does not apply to the phenols and anilines. The

(11) Marsden and Sutton, *J. Chem. Soc.*, 599 (1936).

data for the substituted phenols are presented in Table IV.

TABLE IV

SUBSTITUTED PHENOLS			
$V = 160 \text{ \AA.}^3$	$R = 5.1 \text{ \AA.}$	$D_E = 6.5$	
Phenol	ΔpK (obsd.)	ΔpK (calcd.)	$M_{int.}$ in D
<i>p</i> -Cresol ^a	-0.25	-0.10	0.00 ^b
<i>p</i> -Chlorophenol ^a	.50	.50	-.03 ^b
<i>p</i> -Hydroxybenzaldehyde ^a	1.30	.45	Large ^c
<i>p</i> -Cyanophenol ^a	2.05	1.30	Probably large ^d
<i>p</i> -Nitrophenol ^a	2.80	1.25	0.71 ^b
Hydroquinone ^a	-0.70	-0.05	

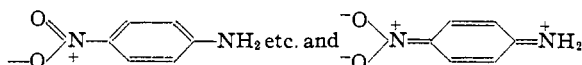
^a Landolt-Börnstein, "Physikalisch-chemische Tabellen."

^b Marsden and Sutton, ref. 11. ^c The observed moment in solution of *p*-hydroxybenzaldehyde of 4.19 D (Pearce and Berhenke, *J. Phys. Chem.*, **39**, 1005 (1935)) considerably exceeds 3.20, the moment calculated on the basis of free rotation of both groups. ^d While no value for the interaction moment is available for *p*-cyanophenol, the interaction moment for *p*-cyanodimethylaniline is known. While exceeded by that of *p*-nitrodimethylaniline (1.86 D) it is none the less large (0.71 D).

In the case of the phenols, while the electrostatic theory adequately accounts for the effect of halogen substituents, the effect of the nitro group, for example, in increasing the strength of phenol, is much greater than can be accounted for on the basis of the group moment alone.

It is an interesting and significant fact that, in the majority of cases in which the electrostatic theory is inadequate, the dipole moment of the molecule is not equal to the vector sum of the constituent dipoles. When there is no interaction of the substituent groups, such a summation is valid.¹²

The classical case of interaction of substituent groups is that of para nitroaniline, where the dipole moment of the compound is greater than the absolute sum of the constituent dipoles. Such an enhanced moment has been explained by the assumption that para nitroaniline is a resonance hybrid¹³ of the following structures



The last column of Table IV gives the interaction moment for the substituted phenols. The correspondence between the interaction moment and the deviations from the electrostatic theory are apparent.

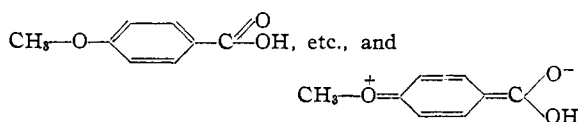
It is reasonable to assume that resonance is more pronounced in the substituted phenolate ion than

(12) Höjendahl, *Physik. Z.*, **30**, 391 (1929).

(13) Kümmler and Porter, *THIS JOURNAL*, **56**, 2549 (1934).

in the phenol itself. On this basis, it can be anticipated that, in those cases in which there is interaction of the groups in para positions, the substituent will increase the acid strength of phenol more than can be predicted from a purely electrostatic treatment.

A similar explanation can be advanced to account for the large decrease of acidity caused by a methoxyl or hydroxyl substituent in benzoic acid. The resonating forms of the para methoxy acid are the following



Here it is reasonable to assume that resonance is more important in the acid than in the corresponding ion. As yet, there are no dipole moment data available to support the assumption of resonance in para methoxybenzoic acid. Further, no explanation of the anomalous behavior of hydroquinone can be offered at this time.

Table V contains the data for substituted anilines, regarding anilinium ion as an acid according to the Brönsted definition. Included are the cases of benzidine and *p*-phenylenediamine, in which the substituent is a charged group.

TABLE V
SUBSTITUTED ANILINES

Aniline	V in Å. ³	R in Å.	D_E	ΔpK (obsd.)	ΔpK (calcd.)	$M_{int.}$
<i>p</i> -Phenylene- diamine	190	5.6	34	2.90	1.25	
<i>p</i> -Benzidine	250	9.9	94	0.60	0.25	
<i>p</i> -Toluidine	165	5.1	6.2	-0.50	-0.10	0.00
<i>p</i> -Chloroaniline	165	5.1	6.2	.50	.50	.06
<i>p</i> -Bromoaniline	165	5.1	6.2	.35	.50	.05
<i>p</i> -Nitroaniline	165	5.1	6.2	3.45	1.25	.95
<i>p</i> -Anisidine	165	5.1	6.2	-.70	-.10	

While it is at once obvious that the electrostatic equations are quite inadequate to account for the base strength of the substituted anilines, it seems likely that differences in resonance energy can account for many of the observed effects.

Finally, it is interesting to consider the computations in this paper in the light of Hammett's¹⁴ empirical equation

$$\log K = \log K^0 + sr$$

where K is any rate or equilibrium constant for a substituted benzene derivative, K^0 is the corre-

sponding constant for the unsubstituted benzene derivative, s is a constant characteristic of the substituent, and r , a constant characteristic of the reaction, has been set equal to unity for the case of the ionization of substituted benzoic acids. Hammett's equation is of much broader scope than the present treatment, and includes both those effects ascribed to resonance and the purely electrostatic ones. It is interesting that a special value of s was reserved for the *p*-nitro group in aniline and phenol, cases in which the interaction ascribed to resonance is especially large. The present treatment can predict the s values of Hammett's equation with moderate accuracy for those substituents for which no large resonance effects have been observed. The calculated constants are the computed values of ΔpK for the benzoic acids. They have the proper sign, are in the correct sequence and of the right order of magnitude; while the agreement is far from perfect, it is significant that a theoretical treatment based on the electrostatic theory can even approximate these constants.

TABLE VI

Para substituent	VALUES OF s	
	s (Hammett)	s (calcd.)
CH ₃	-0.17 ± 0.05	-0.06
F	+ .06 ± .07	+ .24
Cl	+ .23 ± .04	+ .27
Br	+ .23 ± .04	+ .26
NO ₂	+ .78 ± .07	+ .65
CN	+1.00 ± .04	+ .68

Summary

The electrostatic effect of substituents on the dissociation constants of para substituted phenyl acetic acids, benzoic acids, phenol and anilines has been computed by the method of Kirkwood and Westheimer. It is found that the electrostatic effect is the predominant factor in determining the strength of the carboxylic acids with the exception of the para hydroxy and methoxy benzoic acids. The electrostatic effect is an important but subordinate cause of the variation of acidity among substituted phenols and anilinium ions. The difference between the electrostatic and the total effect of a substituent is greatest in those cases in which resonance interaction of the groups has already been indicated by considerations of dipole moment data.

CHICAGO, ILLINOIS

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(14) Hammett, *THIS JOURNAL*, **59**, 96 (1937).