

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Acidic Dissociation Constants of Phenoxyacetic Acid and its Derivatives

BY NORMAN V. HAYES AND GERALD E. K. BRANCH

Introduction

The dissociation constants of the derivatives of an aromatic acid are generally related to each other in much the same way as those of the corresponding derivatives of another aromatic acid. In some cases the correspondence is very striking, in others it is practically lacking. The reasons for these similarities and anomalies in the effects of groups are far from being fully understood, and it seems to be important to increase our knowledge of the facts. There are many ways of doing this, including the mere extension of the classes of acids for which there are ample data.

The dissociation constants of few of the derivatives of phenoxyacetic acid have been measured. For this reason, we decided to measure the dissociation constants of as many derivatives of phenoxyacetic acid as time permitted, concentrating on ortho, meta and para mono derivatives. We were able to measure the strengths of phenoxyacetic acid and twenty-four of its mono derivatives.

This collection of data has the advantage that all the measurements were obtained in the same way and with the same apparatus. This is important in the present case, because the dissociation constants of this class of acids do not have a wide spread.

The collection includes redeterminations of previously measured constants. There are some unfortunate omissions. No amino or carbonyl derivative is included. We never reached the latter type of compound, but deliberately side-stepped the former. After correcting for the zwitter-ion effect, one cannot hope to obtain the dissociation constant of an amino-phenoxyacetic acid with anything like the accuracy of the rest of the data.

Preparation and Purification of the Acids

All the acids were prepared by the same general procedure. The appropriate phenol, chloroacetic acid and sodium hydroxide in the molal proportions 1:1:2 were dissolved in the minimum amount of water. The solution

TABLE I
EQUIVALENT WEIGHTS AND MELTING POINTS OF THE ACIDS

Acid	Equivalent weight		Melting points, °C.		Literature
	Theoretical	Experimental	Observed (cor.)		
$C_6H_5OCH_2COOH$	152.2	152.3	99.0-99.1	96, 97, 98-99	
<i>o</i> -NO ₂ C ₆ H ₄ OCH ₂ COOH	197.1	197.0	158.2-158.5	156.5	
<i>m</i> -NO ₂ C ₆ H ₄ OCH ₂ COOH	197.1	197.3	156.4-156.7	151, 154.5	
<i>p</i> -NO ₂ C ₆ H ₄ OCH ₂ COOH	197.1	197.1	187.2-187.5	184	
<i>o</i> -CH ₃ C ₆ H ₄ OCH ₂ COOH	166.2	166.6	156.8-157.4	151-152	
<i>m</i> -CH ₃ C ₆ H ₄ OCH ₂ COOH	166.2	166.5	103.0-103.5	102-103	
<i>p</i> -CH ₃ C ₆ H ₄ OCH ₂ COOH	166.2	166.3	138.2-138.7	134-136	
<i>o</i> -CH ₃ OC ₆ H ₄ OCH ₂ COOH	182.2	182.3	121.0-121.4	116, 121	
<i>m</i> -CH ₃ OC ₆ H ₄ OCH ₂ COOH	182.2	182.4	115.5-115.9	111-113, 115-118	
<i>p</i> -CH ₃ OC ₆ H ₄ OCH ₂ COOH	182.2	182.1	110.5-111.0	110-112	
<i>o</i> -IC ₆ H ₄ OCH ₂ COOH	278.1	278.4	135.5-136.0	134-135	
<i>m</i> -IC ₆ H ₄ OCH ₂ COOH	278.1	278.2	115.4-115.6	114-115.5	
<i>p</i> -IC ₆ H ₄ OCH ₂ COOH	278.1	278.4	159.5-160.0	154-156	
<i>o</i> -BrC ₆ H ₄ OCH ₂ COOH	231.1	231.2	144.1-144.5	141-143	
<i>m</i> -BrC ₆ H ₄ OCH ₂ COOH	231.1	231.6	108.5-108.8	107-108.5	
<i>p</i> -BrC ₆ H ₄ OCH ₂ COOH	231.1	231.5	161.4-161.8	157	
<i>o</i> -ClC ₆ H ₄ OCH ₂ COOH	186.6	186.9	147.2-147.7	143-145	
<i>m</i> -ClC ₆ H ₄ OCH ₂ COOH	186.6	187.0	109.7-110.2	108-110	
<i>p</i> -ClC ₆ H ₄ OCH ₂ COOH	186.6	186.7	156.7-157.2	155-156.5	
<i>o</i> -FC ₆ H ₄ OCH ₂ COOH	170.1	170.5	139.1-139.5	...	
<i>m</i> -FC ₆ H ₄ OCH ₂ COOH	170.1	170.0	111.3-111.7	...	
<i>p</i> -FC ₆ H ₄ OCH ₂ COOH	170.1	170.3	104.2-104.6	...	
<i>o</i> -CNC ₆ H ₄ OCH ₂ COOH	177.2	177.5	183.4-183.8	...	
<i>m</i> -CNC ₆ H ₄ OCH ₂ COOH	177.2	177.4	192.1-192.6	...	
<i>p</i> -CNC ₆ H ₄ OCH ₂ COOH	177.2	177.3	178.2-178.5	...	
2,6-(CH ₃) ₂ C ₆ H ₃ OCH ₂ COOH	180.2	180.6	128.7-129.0	...	
3-NO ₂ , 4-ClC ₆ H ₃ OCH ₂ COOH	231.6	231.6	138.1-138.5	...	

was heated for three to six hours at 100°. After cooling, the solution was acidified and the acid extracted with ether, and then re-extracted from the ether with a dilute solution of sodium carbonate. The phenoxyacetic acid was precipitated from the alkaline solution with hydrochloric acid. The crude product was recrystallized from water until no further change in the melting point could be observed.

The purity of the product was established by a determination of the equivalent weight and a comparison of the melting point with that given in the literature. These data are shown in Table I. In general, our melting points are a little higher than those previously reported, which suggests a more than average degree of purity. The equivalent weights of all of our products agree with the theoretical within 0.3%. The average agreement between observed and theoretical equivalent weights is 0.12%. It is reasonable to claim that all our products are within 0.5% of being pure.

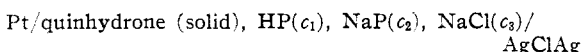
We found no reference to some of the acids that we prepared. These compounds were analyzed for carbon and hydrogen; the results are shown in Table II. The percentages given are the mean values of duplicate determinations. These analyses in conjunction with the equivalent weights leave no doubt as to the identities of the compounds.

TABLE II
CARBON AND HYDROGEN DETERMINATION

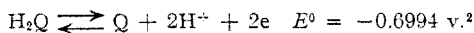
Acid	Calcd.		Experimental	
	C, %	H, %	C, %	H, %
<i>o</i> -FC ₆ H ₄ OCH ₂ COOH	56.47	4.14	56.34	4.06
<i>m</i> -FC ₆ H ₄ OCH ₂ COOH	56.47	4.14	56.57	4.11
<i>p</i> -FC ₆ H ₄ OCH ₂ COOH	56.47	4.14	56.46	4.25
<i>o</i> -CNC ₆ H ₄ OCH ₂ COOH	61.01	3.98	61.07	3.92
<i>m</i> -CNC ₆ H ₄ OCH ₂ COOH	61.01	3.98	61.04	3.92
<i>p</i> -CNC ₆ H ₄ OCH ₂ COOH	61.01	3.98	60.94	3.89
2-CH ₃ -6-CH ₃ C ₆ H ₃ OCH ₂ COO	66.65	6.71	66.57	6.60
3-NO ₂ -4-ClC ₆ H ₃ OCH ₂ COOH	41.50	2.61	41.54	2.59

Determination of the Dissociation Constants

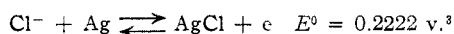
The dissociation constants were measured by an electromotive force method that has been used very successfully by Harned and Ehlers.¹ In this method the cell is



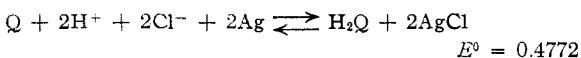
where HP and NaP are the acid and its sodium salt, and c_1 , c_2 and c_3 are concentrations. The electrode reactions and their E^0 values are



and



where Q is quinone. The cell reaction and its E^0 value are



(1) Harned and Ehlers, *THIS JOURNAL*, **54**, 1350 (1932).

(2) Hovorka and Dearing, *ibid.*, **57**, 496 (1935).

(3) Randall and Young, *ibid.*, **50**, 489 (1928).

Harned uses $E^0 = 0.4773$. The difference is not significant.

Harned and Ehlers have shown how the thermodynamic dissociation constant of an acid can be obtained from e. m. f. measurements of these cells at different ionic strengths by extrapolation to zero ionic strength. Their method, which was followed by us, is outlined below.

The e. m. f. of the cell is given by the equation

$$E = E^0 - \frac{RT}{2f} \ln \frac{a_{\text{H}_2\text{Q}}}{a_{\text{Q}}a_{\text{H}^+}^2a_{\text{Cl}^-}^2} \quad (1)$$

Combining this equation with the equality of the concentrations of quinone and hydroquinone, and expressing activity as the product of concentration and activity coefficient one obtains

$$E - 0.4772 - 0.05915 \log_{10} \frac{C_{\text{HP}}C_{\text{Cl}^-}}{C_{\text{P}^-}} = 0.05915 \log_{10} \frac{\gamma_{\text{HP}}\gamma_{\text{Cl}^-}}{\gamma_{\text{P}^-}} - 0.02958 \log_{10} \frac{\gamma_{\text{H}_2\text{Q}}}{\gamma_{\text{Q}}} + 0.05915 \log_{10} K \quad (2)$$

where γ is the activity coefficient and K is the thermodynamic dissociation constant.

The first term on the right-hand side of the equation varies linearly with the ionic strength, becoming zero at zero ionic strength. The second term has been found to vary linearly with ionic strength. It drops out at zero ionic strength since its value is then included in E^0 . Hence values of the left-hand side of the equation when plotted against ionic strength can be extrapolated to give K at zero ionic strength.

However, the ratio of the concentration of HP and P⁻ cannot be exactly determined without knowing K_c , the dissociation constant expressed in concentrations. This difficulty was resolved by Harned and Ehlers by assuming a value for K_c and using it to calculate a value of K , then using this value for K_c to obtain a new value of K , and so on until no further change is obtained in K . The justification for this lies in the equality of K and K_c at zero ionic strength.

The electrodes and cells were very similar to models that have been described previously by other investigators. The silver-silver chloride electrode was made by covering a platinum foil with a paste of seven parts of silver oxide and one part of silver chlorate and baking at 650°. The rest of the cell was similar to that described by Harned and Wright.⁵ The only modification made by us was that an outlet tube, fitted with a

(4) Rule and LaMer, *ibid.*, **58**, 2339 (1936).

(5) Harned and Wright, *ibid.*, **55**, 4849 (1933).

stopcock, was placed near the top of the quinhydrone cell. This allowed us to sweep the cell out with nitrogen, and fill it without allowing any contact with oxygen.

The e. m. f. was measured with a Leeds and Northrup type K potentiometer used in conjunction with a Rubicon lamp and scale galvanometer with a sensitivity of 5×10^{-9} amp./mm. For solutions with very low conductivities a Leeds and Northrup galvanometer with a sensitivity of 1×10^{-10} amp./mm. was used.

The quinhydrone was purified by recrystallization from oxygen-free water. The subsequent drying and storing was done in an atmosphere of nitrogen.

All solutions were prepared by volume. The densities were not determined. However, by assuming the densities of the solutions equal to that of water, we have calculated our dissociation constants with activities expressed in moles per 1000 g. of water. The total normalities of the solutions with respect to the acids, their salts and sodium chloride varied between 0.1 and 0.008, so that an error introduced by not determining the density is in the fourth or fifth significant figure. An experimental error from some other cause is to be expected in the second or third significant figure.

Experimental Results

The dissociation constants that we obtained, and corresponding values given in the literature, are shown in Table III. Our values are shown in the second column, with K defined by the equation $K = a_{\text{H}^+}a_{\text{P}^-}/a_{\text{HP}}$, where a is the activity taken as equal to the molal concentration at zero ionic strength. The constants in the third column are defined by $K_{\text{C}} = C_{\text{H}^+}C_{\text{P}^-}/C_{\text{HP}}$, where C is the molar concentration.

Our values appear to be about 15% lower than the classical dissociation constants, all of which were obtained from conductivity measurements. The check in the values for $o\text{-CH}_3\text{OC}_6\text{H}_4\text{OCH}_2\text{COOH}$ is probably an experimental disagreement. Except for $o\text{-CH}_3\text{O}$ the relative effects of the groups on K and K_{C} are approximately the same.

Comparison of the Dissociation Constants of Phenoxyacetic and Benzoic Acid Derivatives

The quantity $\log K_{\sigma} - \log K_0$, where K_0 is the dissociation constant of an acid and K_{σ} that of another acid derived from the first by substituting a group for a particular hydrogen atom, can be used as a measure of the effect of the group on the

TABLE III
THE DISSOCIATION CONSTANTS OF PHENOXYACETIC ACID AND SOME OF ITS DERIVATIVES IN AQUEOUS SOLUTION, $T = 25^{\circ}$

Acid	$K \times 10^4$	$K_{\text{C}} \times 10^4$ (literature)
$\text{C}_6\text{H}_5\text{OCH}_2\text{COOH}$	6.75	7.56 ^a
$o\text{-CH}_3\text{C}_6\text{H}_4\text{OCH}_2\text{COOH}$	5.93	6.82 ^b
$m\text{-CH}_3\text{C}_6\text{H}_4\text{OCH}_2\text{COOH}$	6.27	6.63 ^b
$p\text{-CH}_3\text{C}_6\text{H}_4\text{OCH}_2\text{COOH}$	6.09	7.03 ^b
$o\text{-CH}_3\text{OC}_6\text{H}_4\text{OCH}_2\text{COOH}$	5.88	5.85 ^b
$m\text{-CH}_3\text{OC}_6\text{H}_4\text{OCH}_2\text{COOH}$	7.22	..
$p\text{-CH}_3\text{OC}_6\text{H}_4\text{OCH}_2\text{COOH}$	6.13	..
$o\text{-NO}_2\text{C}_6\text{H}_4\text{OCH}_2\text{COOH}$	12.7	15.5 ^a
$m\text{-NO}_2\text{C}_6\text{H}_4\text{OCH}_2\text{COOH}$	11.2	..
$p\text{-NO}_2\text{C}_6\text{H}_4\text{OCH}_2\text{COOH}$	12.8	15.0 ^a
$o\text{-NCC}_6\text{H}_4\text{OCH}_2\text{COOH}$	10.6	..
$m\text{-NCC}_6\text{H}_4\text{OCH}_2\text{COOH}$	9.24	..
$p\text{-NCC}_6\text{H}_4\text{OCH}_2\text{COOH}$	11.7	..
$o\text{-FC}_6\text{H}_4\text{OCH}_2\text{COOH}$	8.22	..
$m\text{-FC}_6\text{H}_4\text{OCH}_2\text{COOH}$	8.28	..
$p\text{-FC}_6\text{H}_4\text{OCH}_2\text{COOH}$	7.42	..
$o\text{-ClC}_6\text{H}_4\text{OCH}_2\text{COOH}$	8.90	10.2 ^b
$m\text{-ClC}_6\text{H}_4\text{OCH}_2\text{COOH}$	8.51	..
$p\text{-ClC}_6\text{H}_4\text{OCH}_2\text{COOH}$	7.89	9.62 ^b
$o\text{-BrC}_6\text{H}_4\text{OCH}_2\text{COOH}$	7.53	..
$m\text{-BrC}_6\text{H}_4\text{OCH}_2\text{COOH}$	8.03	..
$p\text{-BrC}_6\text{H}_4\text{OCH}_2\text{COOH}$	7.37	..
$o\text{-IC}_6\text{H}_4\text{OCH}_2\text{COOH}$	6.72	..
$m\text{-IC}_6\text{H}_4\text{OCH}_2\text{COOH}$	7.44	..
$p\text{-IC}_6\text{H}_4\text{OCH}_2\text{COOH}$	6.94	..
$2,6\text{-(CH}_3)_2\text{C}_6\text{H}_3\text{OCH}_2\text{COOH}$	4.41	..
$3\text{-NO}_2\text{-4-ClC}_6\text{H}_3\text{OCH}_2\text{COOH}$	11.0	..

^a Ostwald, *Z. physik. Chem.*, **3**, 418 (1889). ^b Behaghel, *J. prakt. Chem.*, **114**, 287, 312 (1926).

strength of an acid. This quantity depends not only on the substituent group but also on the parent acid and the particular hydrogen atom replaced. However, the relative values of $\Delta \log K_{\sigma}$ for groups in general are often found to be nearly the same for acids belonging to some limited class. In these cases one can assign certain values to the groups and put

$$\Delta \log K_{\sigma} = \sigma \rho \quad (3)$$

where σ is one of these values assigned to a group, and ρ is determined by the parent acid and the position of substitution. One might expect this equation to hold where the effects of the groups can be attributed to a single factor, *e. g.*, the inductive factor, and all the parent acids are closely related in structure. For instance, the work of Hixon and Johns⁶ shows that this equation holds fairly well for the saturated fatty acids.

Hammett⁷ has shown that the equation

$$\Delta \log K_{\sigma} = \sigma \rho \quad (3')$$

(6) Hixon and Johns, *This Journal*, **49**, 1786 (1927).

(7) Hammett, *ibid.*, **59**, 96 (1937).

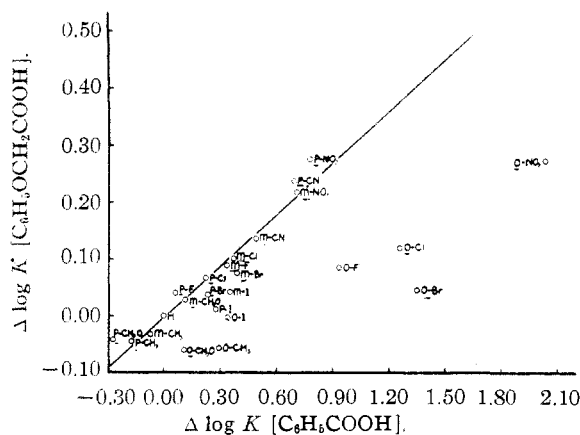


Fig. 1.—A graphical comparison of the effects of substituent groups on the logarithms of the dissociation constants of phenoxyacetic and benzoic acids.

is applicable to meta and para acidic derivatives of benzene, though in these compounds substituent groups can have both inductive and resonance effects. In Hammett's equation the definitions of σ and ρ are somewhat different from those given in the preceding paragraph, σ being determined by both the group and the position of substitution, and ρ by the parent acid alone. Also the relative effects of groups when attached to the benzene ring differ from their relative effects when attached to a saturated carbon chain. This difference is more marked in para than in meta substitutions.

Hammett's equation, like all others of this type, is subject to qualifications. According to the degree of accuracy required it is necessary to limit the class of acids, either with respect to the substituent groups, their positions, or the parent acids. Thus Hammett's equation is not generally applied to ortho derivatives; its accuracy and universality are greater when limited to meta derivatives; with certain para substituents Hammett's equation has significant accuracy only when the aromatic acids are divided into subclasses, each of which has its own value of σ for substituent.⁸ It is to be expected that other anomalies are to be found. Nevertheless we shall use Hammett's equation to compare the effects of groups on the dissociation constant of phenoxyacetic acid with the corresponding effects on the constant of another aromatic acid (benzoic), without any restriction as to the type of substitution. In this way both similarities and anomalies will be apparent.

(8) See the extensive comparison by Branch and Calvin, "Theory of Organic Chemistry," Prentice-Hall, New York, N. Y., 1941, Figs. 36, 37, 38 and 39.

In Fig. 1 we have plotted the *o*-, *m*- and *p*-values of $\Delta \log K_\sigma$ for phenoxyacetic acid against the corresponding values of $\Delta \log K_\sigma$ for benzoic acid, using circles whose diameters correspond to the uncertainties of the measurements on the phenoxyacetic acids. Except for *m*-Br, and *m*-I, the points for *m*-substitutions fall very accurately on a straight line. This line is shown in the figure. We have taken the slope of this line, 0.30, as ρ for phenoxyacetic acid assuming ρ for benzoic acid equal to unity. Using this value of ρ , σ equal to $\Delta \log K_\sigma$ for benzoic acid, and the dissociation constant of phenoxyacetic acid, we have calculated the dissociation constants for the phenoxy-

TABLE IV

OBSERVED AND CALCULATED DISSOCIATION CONSTANTS OF DERIVATIVES OF PHENOXYACETIC ACID

Substituent	$10^4 \times K(\text{C}_6\text{H}_5\text{COOH})$	$10^4 \times K(\text{C}_6\text{H}_4(\text{OCH}_2)\text{COOH})$ (Exp.)	$10^4 \times K(\text{C}_6\text{H}_4(\text{OCH}_2)\text{COOH})$ (Calcd.)
H	6.27	6.75 ± 0.13	(6.75)
Meta Groups			
CH ₃	5.35	6.27 ± .13	6.37
OCH ₃	8.17	7.22 ± .14	7.24
NO ₂	32.1	11.2 ± .2	11.0
CN	19.5	9.24 ± .19	9.42
F	13.6	8.28 ± .17	8.45
Cl	14.8	8.51 ± .17	8.65
Br	15.4	8.03 ± .16	8.75
I	14.1	7.44 ± .15	8.59
Para Groups			
CH ₃	4.24	6.09 ± .12	5.93
OCH ₃	3.38	6.13 ± .12	5.55
NO ₂	37.6	12.8 ± .3	11.6
CN	31.0	11.7 ± .2	10.9
F	7.22	7.42 ± .15	6.99
Cl	10.5	7.89 ± .16	7.84
Br	10.7	7.37 ± .15	7.89
I	...	6.94 ± .14	8.11 ^a
Ortho Groups			
CH ₃	12.3	5.93 ± .12	8.21
OCH ₃	8.06	5.88 ± .12	7.20
NO ₂	671	12.7 ± .3	27.4
CN	...	10.6 ± .2	...
F	54.1	8.22 ± .16	12.9
Cl	114	8.90 ± .18	16.1
Br	140	7.53 ± .15	17.2
I	14.1	6.72 ± .13	8.49
Two Groups			
2-CH ₃ , 6-CH ₃	62.2	4.41 ± .09	13.4
3-NO ₂ , 4-Cl	44.0	11.0 ± .2	11.9

^a This value has been calculated for the value of σ given by Hammett. If the value of $\Delta \log k_\sigma$ for iodobenzoic acid in 50% alcohol obtained by Kuhn and Wassermann, *Helv. Chim. Acta*, **113**, 31 (1928), were used instead, 8.19×10^{-4} would be obtained for the calculated value of the constant for *p*-iodophenoxyacetic acid.

acetic acid derivatives of all types. These calculated values are shown in Table IV, column 4. The experimental values are given in column 3. The dissociation constants of the corresponding derivatives of benzoic acid are given in column 2.

One can make five generalizations from an inspection of Table IV. (1) The calculated dissociation constants of all bromo and iodo derivatives are too high. We shall exempt bromo and iodo derivatives from the other generalizations. (2) The dissociation constants of meta derivatives can be calculated accurately. (3) The dissociation constants of para derivatives can be calculated accurately when the group has no strong resonance interaction with the aromatic nucleus. (4) The calculated dissociation constants of para derivatives are too low, when the group has a strong resonance interaction with the aromatic nucleus, whether the resonances charge the ring positively (NO_2 , CN) or negatively (OCH_3 , F). The discrepancies are definitely greater than the experimental error, but not so large as to make the calculations valueless. (5) The calculated dissociation constants of all ortho derivatives are too high. The errors are large enough to vitiate the method of calculation. Before further discussion of these observations, we shall consider a theoretical basis for Hammett's equation.

Theoretical

Insulated Acids.—In a set of acids, HABCX_1 , HABCX_2 , . . . , where H is a hydrogen atom, X is a variable group, and A, B, C, are constant groups, with B insulating any resonance in HA from any resonance in CX, that part of $\Delta \log K_\sigma$ due to inductive and resonance effects can be attributed to the interaction of two changes of electric charge, one due to substitution of one X for another, and located arbitrarily on the atom in C next to B, and the other due to the ionization, and located arbitrarily on the atom in A next to B. Assuming no other effects, one can write

$$\Delta \log K_\sigma = - \frac{\delta e_\sigma \delta e_1}{2.3 RTd} \quad (4)$$

where δe and δe_1 are the changes of charge mentioned above, and d is an effective distance. The quantities d , δe_1 and δe_σ are determined, respectively, by B, A and the change of CX_1 to CX_2 . If we choose a fixed temperature and HABCH as a reference acid, equation 4 leads to equation 3

$$\Delta \log K_\sigma = \sigma \rho \quad (3)$$

with the same set of σ values used for X groups for all parent acids having C in common.

The definition of C includes the relative position of its bonds to X and B. When no resonance interaction is possible between C and X, the effect of the group decreases in a regular manner with the length of the chain separating X and the point of ionization, and a set of σ values can be assigned to the X groups, while changes in ρ can take care of the position of substitution. But when a resonance interaction between C and X is possible, even the sign of δe_σ can be changed by the position of substitution. Consequently, when C is a benzene ring, ortho, meta and para derivatives belong to three distinct classes of acids, each of which has its own set of σ values for the X-groups. With X = H three classes of acids have a common member, and by assigning three σ values (*o*, *m*, *p*) for each group one can write

$$\Delta \log K_\sigma = \sigma \rho \quad (3')$$

where σ is determined by the group and its position in the benzene ring, and ρ is determined by A and B. Further, σ is proportional to the change in the charge of atom 1 of the ring due to the substitution.

In the above derivation of Hammett's equation the aromatic nucleus has been assumed to be insulated from any resonance of the acidic group. Actually, the equation is applicable to acids in which the benzene ring and the atom from which the proton ionizes are conjugated with the same group (cross-conjugation) or with each other (direct-conjugation). We shall use benzoic acid and phenol, respectively, as examples of cross-conjugation and direct conjugation.

Benzoic Acid.—In benzoic acid the carbonyl group resonates with both the benzene nucleus and the acidic hydroxyl group. The resulting competition reduces the effect of the carboxylic resonance and decreases the acidic strength. But since the structural changes under consideration do not insulate the resonances, $\Delta \log K_\sigma$ for benzoic acid is essentially proportional to the product $\delta e_\sigma \delta e_1$, as it is in an insulated acid. However, the carbon atom of the carboxyl group receives electrons from the phenyl group to a greater extent in the acid than in the ion. Consequently δe_1 is a smaller negative charge for benzoic acid than for an insulated carboxylic acid. Hence the cross-conjugation decreases ρ , but does not affect σ , and Hammett's equation is applicable to this type of acid.⁹

(9) We have neglected the second order effect of σ on the cross-conjugation effect. This is probably not far from proportional to σ , and so cannot appreciably invalidate the proportionality between σ and $\Delta \log K_\sigma$.

The above predicted decrease in σ can be seen in a comparison of the ratios $\rho_{\text{C}_6\text{H}_5\text{CH}_2\text{COOH}} : \rho_{\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{COOH}}$ and $\rho_{\text{C}_6\text{H}_5\text{COOH}} : \rho_{\text{C}_6\text{H}_4\text{CH}_2\text{COOH}}$. The former is 2.8:1, the latter 2.2:1.

The introduction of an atom having a pair of unshared electrons in the ortho or para position in benzoic acid introduces a new resonating structure, *e. g.*, $\text{CH}_2\text{O}^{\oplus}=\text{C}_6\text{H}_4=\text{C}(\text{OH})\text{O}^{\ominus}$. The resulting resonance is in competition with the carboxylic resonance and has a cross-conjugation effect which decreases the acidic strength. This effect is not present in an insulated acid. Hence with such a para substituent, if σ has been evaluated from an insulated acid, then for benzoic acid

$$\Delta \log K_{\sigma} = \sigma\rho - \alpha \quad (5)$$

where ρ is the value attributed to benzoic acid for other substitutions, and $-\alpha$ is the cross conjugation effect of the group. One can maintain the form of Hammett's equation by subtracting α/ρ from σ . In that case anomalies would appear in the strengths of the insulated acids, where their magnitudes are smaller. When the acids are of very similar type (*e. g.*, benzoic and phenylboric) cross-conjugation effects are proportional to ρ , and a single σ -value can be assigned not only to the substitutions that give an extra cross-conjugation, but also to structural changes that remove the cross-conjugation effect of the phenyl group (*e. g.*, interpolation of CH_2).

Cross-conjugation effects are not large, and an α -value is necessary only when the substitution introduces a strong resonance. The groups that give important cross-conjugation effects are hydroxyl, alkoxyl, amino, and the fluorine atom.

Phenol.—Phenolic resonance ($\text{C}_6\text{H}_5\text{OH}$, $\text{C}_6\text{H}_5=\text{O}^{\oplus}\text{H}$) implies a degree of double-bondedness between the oxygen atom and carbon atom (1) of the aromatic nucleus. To obtain the extra bonding, carbon atom (1) acts in the tricovalent

state, $\text{a}-\overset{\text{b}}{\underset{\text{c}}{\text{C}}}-\text{c}$. The energy is approximately proportional to the tricovalency. The quantity σ is a measure of the change of tricovalency of carbon atom (1) resulting from substitution in an insulated aromatic acid. As a first approximation one can then put the change of the phenolic resonance energy due to a substitution as proportional to σ for the substitution. Since this applies to both the phenol and its ion, the change in $\log K$ due to the effect of substitution on phenolic resonance is

proportional to σ , and, when the whole change in $\log K$ can be attributed to resonance and inductive effects, $\Delta \log K = \sigma\rho$.

In the above paragraph a resonance interaction between a substituent group and the aromatic nucleus has been assumed not to interfere with, nor to be enhanced by, the phenolic resonance. This assumption is warranted when the substituent and acidic groups are meta to each other, but it involves definite errors when strongly resonating groups are ortho or para to the acidic group. A resonance in which an ortho or para group gives electrons to the ring interferes with the phenolic resonance, and a cross-conjugation effect similar to that in benzoic acid results. A resonance in which an ortho or para group accepts electrons from the ring is enhanced by the phenolic resonance.

This enhancement of the resonance can be attributed to the existence of a resonating structure in the substituted phenol that belongs to a type that is present in neither the unsubstituted phenol, nor in a similarly substituted insulated acid. This type of structure is characterized by the aromatic ring being doubly bonded to both the acidic and substituent groups. A typical example

is $\text{HO}-\text{C}_6\text{H}_4=\text{N}(\text{O}^{\ominus})_2$. Since this type of structure contributes more to the resonance of the ion than to that of the acid, a group that permits it increases the strength of a phenol more than would be expected from its effect on the strength of an insulated acid. For substituted phenols of this type one can write

$$\Delta \log K_{\sigma} = \sigma\rho + \beta \quad (6)$$

where ρ is determined from the effects of meta groups on phenol, and σ from the effect of the substituent group on the strength of an insulated acid.

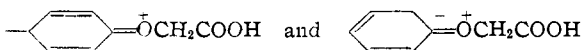
Again one can artificially maintain the form of Hammett's equation by adding β/ρ to σ . This device is useful because β/ρ for a group is the same for phenol as for anilinium ion.

ortho Groups.—When a group is in the *o*-position, there is in general a steric effect. There is no connection between this effect and the change of charge on atom (1) of the aromatic nucleus. Hence there is no reason why, if the effect is expressed as a term in $\Delta \log K_{\sigma}$ and divided by ρ , the quotient should be the same for all parent acids. Therefore, Hammett's equation can be applied to *o*-substitutions only to the ex-

tent that steric effects are negligible. Actually it appears that the steric effects may be greater than those due to resonance and induction.

Charged Groups.—The direct effect of a group cannot be attributed to a change in carbon atom (1) of the nucleus. That Hammett's equation is as accurate as it is for *m*- and *p*-electrically neutral groups indicates that the effect of such groups is chiefly conducted by induction and resonance. A much larger part of the effect of an electrically charged group would be due to the direct effect, and for such groups Hammett's equation would be in error. Thus $\Delta \log K_{p\text{-CO}_2^-(\text{C}_6\text{H}_5\text{COOH})}$ is -0.2 , after correction for the divalence of the ion, but $\Delta \log K_{p\text{-CO}_2^-(\text{C}_6\text{H}_5\text{BO}_2\text{H}_2)}$ is negligible, although $\rho_{\text{C}_6\text{H}_5\text{BO}_2\text{H}_2} > \rho_{\text{C}_6\text{H}_5\text{COOH}}$.¹⁰

Phenoxyacetic Acid.—In phenoxyacetic acid there is no part of the carboxyl group conjugated with the aromatic nucleus, and in that sense phenoxyacetic acid is an insulated aromatic acid. However, there is an additional resonance due to the structures



This resonance increases the strength of the acid.

The introduction of a group into the benzene ring has a two-fold effect. One of these is the same as the effect of introducing the group in an insulated acid; the other is an additional effect due to the change in the above resonance. The additional effect is similar to that of the substitution on the strength of phenol. The total effect is given by the equation

$$\Delta \log K_\sigma = \rho_1 \sigma + \rho_2 \frac{\Delta \log K_\sigma(\text{C}_6\text{H}_5\text{OH})}{\rho_{\text{C}_6\text{H}_5\text{OH}}} \quad (7)$$

meta Derivatives.—For meta and non-resonating para groups, Hammett's equation holds for insulated acids, benzoic acid and phenol without any additional terms or changes in σ . Equation 7 can then be written as

$$\begin{aligned} \Delta \log K_\sigma &= \rho_1 \Delta \log K_\sigma(\text{C}_6\text{H}_5\text{COOH}) + \rho_2 \Delta \log K_\sigma(\text{C}_6\text{H}_5\text{COOH}) \\ &= \rho \Delta \log K_\sigma(\text{C}_6\text{H}_5\text{COOH}) \end{aligned} \quad (8)$$

putting $\rho_{\text{C}_6\text{H}_5\text{COOH}} = 1$. Hence in the absence of other than resonance and inductive effects, the dissociation constants of meta and non-resonating para derivatives of phenoxyacetic acid can be calculated from the dissociation constants of the corresponding derivatives of benzoic acid by Hammett's equation.

One can obtain an approximate idea of the values of ρ_1 and ρ_2 of equation (8). The polariza-

bilities of the structures $-\text{O}-$ and $-\text{CH}_2-$ are approximately the same in the absence of resonance. From this it follows that ρ_1 is approximately equal to $\rho_{\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{COOH}}$, and ρ_1 and ρ_2 are approximately equal to each other and to 0.15.

para Derivatives.—When the resonance of a para group increases the electron density of the aromatic group (*p*-OCH₃ and *p*-F), there is a cross-conjugation in the corresponding derivatives of both phenol and benzoic acid. By making the assumption that the cross-conjugation terms in $\Delta \log K_\sigma$ are proportional to ρ for the parent acid, equation (7) can be changed to

$$\Delta \log K_\sigma = \rho \Delta \log K_\sigma(\text{C}_6\text{H}_5\text{COOH}) + \rho_1 \alpha \quad (9)$$

where $-\alpha$ is the cross-conjugation term for benzoic acid. The dissociation constant of the derivative of phenoxyacetic acid calculated by Hammett's equation will be too low by $\rho_1 \alpha$.

The assumption of proportionality between α and ρ is not verified by experiment, but it is not much in error.

When the resonance of a para group tends to take electrons from the aromatic nucleus (*p*-NO₂ and *p*-CN), there is an extra acid strengthening resonance in the corresponding phenol, but not in the corresponding derivative of benzoic acid. Equation 7 then reduces to

$$\Delta \log K_\sigma = \rho \Delta \log K_\sigma(\text{C}_6\text{H}_5\text{COOH}) + \frac{\rho_2 \beta}{\rho_{\text{C}_6\text{H}_5\text{OH}}} \quad (10)$$

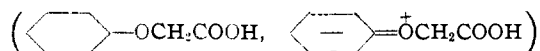
where β is the term for the extra resonance in this type of substituted phenol. The dissociation constant calculated by Hammett's equation will be too low by $\rho_2 \beta / \rho_{\text{C}_6\text{H}_5\text{OH}}$.

The dissociation constants of para derivatives of phenoxyacetic acid calculated from equations 7, 9 and 10, and our estimate of the relative values of ρ_1 and ρ_2 , agree satisfactorily with the observed values. As an example of these calculations we shall use *p*-nitrophenoxyacetic acid. The value of β for *p*-nitrophenol is 0.56. Using Branch and Calvin's value of $\rho_{\text{C}_6\text{H}_5\text{OH}} = 2.56$, and $\rho_2 = 0.15$, $K_{p\text{-NO}_2\text{C}_6\text{H}_4\text{OCH}_2\text{COOH}} = 1.25 \times 10^{-3}$, Hammett's value for $\rho_{\text{C}_6\text{H}_5\text{OH}}$ leads to $K_{p\text{-NO}_2\text{C}_6\text{H}_4\text{OCH}_2\text{COOH}} = 1.30 \times 10^{-3}$. The observed value is 1.28×10^{-3} .

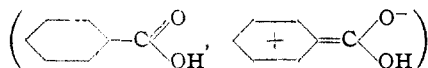
Ortho Derivatives.—We have seen that the steric effects of ortho groups invalidate Hammett's equation. This does not necessitate that, in a plot of $\Delta \log K_\sigma$ of one acid against that of another, the points for ortho groups shall cover the field in a haphazard way. Some factor may

(10) Bettman, Branch and Yabroff, *THIS JOURNAL*, **56**, 1865 (1934).

operate in a similar way for all derivatives. In the comparison of the phenoxyacetic and benzoic acid ortho derivatives the steric hindrance to the resonances



and



is a constantly operating factor. The former resonance increases the strength of the acid and the latter decreases it. Hence the hindrances to these resonances by ortho groups decrease the strengths of the phenoxyacetic acids and increase those of the benzoic acids. This amply accounts for the observation that the value calculated for the dissociation constant of an ortho phenoxyacetic acid from the corresponding derivative of benzoic acid is always too high.

The steric hindrance of ortho groups also affects the value of ρ . As we have seen in the previous discussion the characteristic resonance of benzoic acid tends to decrease ρ while that of phenoxyacetic acid increases ρ . The steric hindrances reduce these effects, so that $\rho_{o\text{-C}_6\text{H}_4\text{COOH}}/\rho_{o\text{-C}_6\text{H}_4\text{OCH}_2\text{COOH}}$ is greater than $\rho_{m\text{-C}_6\text{H}_4\text{COOH}}/\rho_{m\text{-C}_6\text{H}_4\text{OCH}_2\text{COOH}}$.

Neglecting the differences in the steric effects of different groups, these ideas lead to the equation

$$\Delta \log K_{\sigma(o\text{-C}_6\text{H}_4\text{OCH}_2\text{COOH})} = \rho' \Delta \log K_{\sigma(o\text{-C}_6\text{H}_4\text{COOH})} - H \quad (11)$$

where H is a constant and ρ' is less than ρ for meta substitutions. This equation fits surprisingly well with $H = 0.1$ and $\rho' = 0.18$. The calculated and observed values are shown in Table V. The bromo and iodo derivatives are not included in this table. The dissociation constant of *o*-cyano-benzoic acid appears not to have been measured.

TABLE V

RECALCULATION OF THE DISSOCIATION CONSTANTS OF ORTHO DERIVATIVES

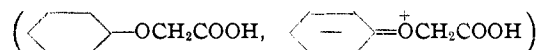
Ortho group	$10^8 \times$	$10^4 \times$	$10^4 \times$
	$K(\text{C}_6\text{H}_4\text{COOH})$	$K(\text{C}_6\text{H}_4\text{OCH}_2\text{COOH})$ Obs.	$K(\text{C}_6\text{H}_4\text{OCH}_2\text{COOH})$ Calcd.
H	6.27	6.75	(6.75)
CH ₃	12.3	5.93	6.05
OCH ₃	8.06	5.88	5.61
NO ₂	671	12.7	12.5
F	54.1	8.22	7.90
Cl	114	8.90	9.04

The agreement between calculated and observed values in Table V indicates that there can be no strong chelation effect in any of the benzoic or

phenoxyacetic derivatives included. A calculation of the dissociation constant of *o*-hydroxyphenoxyacetic acid from that of salicylic acid would certainly be in error.

The effects of ortho groups are often more extreme in di-ortho than in mono-ortho derivatives. We therefore measured the dissociation constant of dimethylphenoxyacetic acid. The second methyl group produces a much greater fractional decrease in the dissociation constant than the first methyl group does. The *o*-methyl derivatives of benzoic acid are stronger than benzoic, but, as in the case of the phenoxyacetic acids, the second *o*-methyl group produces a much greater effect than the first does. The result of this is that a value for the dissociation constant of 2,6-dimethylphenoxyacetic acid calculated by Hammett's equation from the constant of 2,6-dimethylbenzoic acid is very much greater than that observed.

The value obtained for the dissociation constant of 2,6-dimethylphenoxyacetic acid shows that the resonance is reduced but not removed



by the prevention of coplanarity. Without this resonance $\log K$ for phenoxyacetic acid would be that of an α -alkoxy- β -phenylacetic acid, and $\log K$ for the methyl derivatives slightly smaller. This gives an estimate for $\log K$ between -3.7 and -3.8 . The values for phenoxyacetic and 2,6-dimethylphenoxyacetic acids are -3.17 and -3.35 . The resonance effect is reduced by about thirty per cent.

When a substituent group resonates with the ring, a group ortho to it decreases the resonance, and the combined effects of the groups are not additive, but include an ortho effect even though neither group is ortho to the acidic part of the molecule. As an example of this steric effect we measured the dissociation constant of 3-nitro-4-chlorophenoxyacetic acid, and found that $\Delta \log K_{\sigma}$ is markedly less than the sum of the $\Delta \log K_{\sigma}$ values for *m*-nitro and *p*-chloro substitutions. This is also true for 3-nitro-4-chlorobenzoic acid. However, the calculation of the dissociation constant of 3-nitro-4-chlorophenoxyacetic acid from that of the corresponding benzoic acid derivative gives a value that is 8% high. The reason for this is obscure. It suggests that the lack of additivity is not entirely due to the steric hindrance of the resonance of the nitro group.

The $\Delta \log K_p$'s for the halogens do not have a fixed order, but depend on the parent acids and the positions of substitution. Generally two factors are considered, an inductive one by which electrons are drawn to the halogen, and a resonance in which the halogen is an electron donor. The order $F > Cl > Br > I$ is usually assigned to both factors, and the vagaries attributed to variation in the relative importance of the inductive and resonance factors. The failure to calculate the dissociation constants of the bromo and iodo derivatives of phenoxyacetic acid from those of the corresponding derivatives of benzoic acid is a good, but not a unique, example of the inadequacy of considering only the inductive and resonance effects. Presumably other factors become equally important as the size of the atom increases, and these factors do not give effects that are proportional to ρ .

One such factor is polarizability. The effect depends on how the magnitude, not the sign, of the electric field acting on the substituent group changes with dissociation of the proton. Hence the term in $\log K_p$ due to the polarizability of a substituent group cannot be proportional to the ρ of the parent acid. However, the anomalies of the effects of bromine and iodine on the dissociation constant of phenoxyacetic acid cannot be attributed to the polarizability of these atoms. This can be seen by comparing the relative strengths of the *m*-bromo and *m*-fluoro derivatives of a variety of acids. The *m*-bromo derivatives of phenylacetic acid, benzoic acid, phenol and anilinium ion are all stronger acids than their respective *m*-fluoro derivatives. On the other hand, *m*-fluorophenoxyacetic acid is stronger than *m*-bromophenoxyacetic acid. A similar observation is true of the para derivatives. The acids in which the bromo derivative is the stronger acid include an insulated acid, one with a resonance charging the phenyl group positively, two in which resonance charges the ring negatively, and one in which the dissociation of the proton decreases the magnitude of the charge on the molecule. It does not seem reasonable that in all of these acids the dissociation of the proton increases the magnitude of the field on the group, but that in phenoxyacetic acid ionization decreases the magnitude of this field.

In the comparison of acid strengths anomalies may arise, because an arbitrary choice of solvent and temperature has been made. Such an ex-

planation does not seem adequate in the present case in which the anomalies appear in meta and para bromo and iodo compounds but not in other meta and para derivatives.

It would seem that the effects of bromine and iodine include a factor whose nature is as yet unknown. It is probably concerned with the large number of electron shells in the atoms, and would also be operative in the effects of arsenic and selenium atoms and to a less extent in those of phosphorus, sulfur and chlorine atoms. It is probable that there are acids in which this factor is more important than in phenoxyacetic acids. In any case the effect of this obscure factor is not proportional to ρ for the parent acid.

The anomalous weakness of the bromo and iodo derivatives is always more pronounced in the iodo than in the bromo compound. This does not appear in the case of ortho derivatives when the calculated and observed values are compared. The reason for this is that the constant for *o*-iodophenoxyacetic acid is calculated from that of *o*-iodobenzoic acid, which is anomalously weak. Unless one were to assume that there is no steric hindrance in *o*-iodobenzoic acid, one cannot explain the weakness of this acid on inductive and resonance factors alone.

Behaghel and Rollman¹¹ have measured the dissociation constants of $C_6H_5SCH_2COOH$, $C_6H_5SeCH_2COOH$ and some of their derivatives. Their work is sufficiently extensive to permit an estimate of 0.40 and 0.35 ρ for the thio and seleno acids, respectively. The series $C_6H_5OCH_2COOH$, $C_6H_5SCH_2COOH$ and $C_6H_5SeCH_2COOH$ has a maximum in ρ at the thio acid. There are two factors operative on the transmission of the effect of a group in the benzene ring across the oxygen, sulfur or selenium atom, namely, the polarizability of the atom (ρ_1) and the resonance with the benzene ring (ρ_2). In going from oxygen to sulfur the polarizability increases but the resonance decreases. The opposition of these factors can account for the maximum value of ρ .

Summary

The dissociation constants of phenoxyacetic acid and twenty-six of its derivatives were measured, and compared with those of benzoic acid and its corresponding derivatives.

Excepting bromo and iodo compounds, it was

(11) Behaghel and Rollman, *J. prakt. Chem.*, **114**, 287 (1926); *Ber.*, **62B**, 2693 (1929).

found (a) that the dissociation constants of meta derivatives of phenoxyacetic acid can be calculated from those of the corresponding derivatives of benzoic acid by Hammett's equations, (b) that similarly calculated constants for para derivatives are slightly low, when the substituent resonates strongly with the aromatic nucleus, and (c) that similarly calculated constants for all ortho derivatives are too high.

These observations have been explained on the basis of the difference in the types of resonance existing in phenoxyacetic and benzoic acids.

The bromo and iodo phenoxyacetic acids were found to be anomalously weak. It has been pointed out that these anomalies cannot be adequately explained by inductive, resonance, and polarizability effects alone.

BERKELEY, CALIF.

RECEIVED MARCH 22, 1943

[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY OF WESTERN RESERVE UNIVERSITY]

A Simple Approximate Relation between Successive Dissociation Constants of Symmetrical Inorganic Oxygen Acids

BY TERRELL L. HILL

It is well known¹⁻⁶ that, in the absence of interactions between groups, the successive dissociation constants of a symmetrical acid containing n equivalent acidic groups⁷ (n being the *maximum* number of equivalent proton positions—see below) are related by the expression

$$K_j = (n - j + 1)K^0/j \quad j = 1, 2, \dots, n \quad (1)$$

where K^0 is a constant. Thus

$$K_j/K_{j+1} = (j + 1)(n - j + 1)/j(n - j) \quad j = 1, 2, \dots, n - 1 \quad (2)$$

We may call this a zero-th approximation, and it certainly leads to results far from the truth, having neglected the important effects of charges in the molecules, dipole-proton interactions and resonance.

If we consider acids in which resonance and dipole-proton interactions⁸ may be neglected, and use as a model⁵ an acid B in which there is an atom A (the single center of symmetry), with a (formal) charge⁸ z , and about which atom there are distributed n equivalent OH groups, then a treatment of the electrostatic interaction of approximately the same order of refinement as that

of Kossiakoff and Harker⁵ and of Kirkwood and Westheimer⁹ leads, as a first approximation, to

$$K_j/K_{j+1} = (j + 1)(n - j + 1)\alpha/j(n - j), \\ \alpha = e^{\epsilon z/DkT}, \quad j = 1, 2, \dots, n - 1 \quad (3)$$

and

$$\frac{(n - 1)K_1}{2nK_2} = \frac{2(n - 2)K_2}{3(n - 1)K_3} = \frac{3(n - 3)K_3}{4(n - 2)K_4} = \dots = \frac{(n - 1)K_{n-1}}{2nK_n} \quad (4)$$

where ϵ is the protonic charge, D is an effective dielectric constant⁹ and r is the distance between a negatively charged oxygen and a dissociable proton (both D and r are assumed the same, in this first approximation, for B and the ions of B). It is probably not worth while to give the derivation of equation 3 in detail since the general procedure is not new.

Equation 4 does not provide a method for predicting dissociation constants of such generality as other methods,^{4,5} but it has the advantage of involving only a very simple calculation where it is applicable. That is, here we calculate a dissociation constant from two other known constants of the same acid series (*e. g.*, H_3PO_4 , $H_2PO_4^-$, etc.). Other methods allow the calculation of any constant after certain general parameters are adjusted (which adjustment is itself done by making use of measured dissociation constants).

Although equation 4 is restricted to symmetrical⁷ acids in which, as a first approximation, resonance can be neglected, it is more general than might appear at first glance. That is, it includes

(9) J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, **6**, 506 (1938).

(1) E. Q. Adams, *THIS JOURNAL*, **38**, 1503 (1916).
 (2) H. S. Simms, *ibid.*, **48**, 1239 (1926).
 (3) A. L. von Muralt, *ibid.*, **52**, 3518 (1930).
 (4) G. E. K. Brauch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941.
 (5) A. Kossiakoff and D. Harker, *THIS JOURNAL*, **60**, 2047 (1938).
 (6) N. Bjerrum, *Z. physik. Chem.*, **106**, 219 (1923).
 (7) Although this does not exclude acids of the type H_4O^{++} , NH_4^+ , etc., only oxygen acids will be considered here. A treatment similar to the one to be mentioned below leads to an analogous result for symmetrical hydrogen acids, but the corresponding simple model which must be employed is apparently not adequate in this case.
 (8) The effects of dipole-proton interactions normally cancel in taking ratios between successive dissociation constants, since the same interaction is present in all acids of the series. The same is true of a charge on the central atom of the acid.