THE STRUCTURE OF DICARBOXY COMPOUNDS FROM DISSOCIATION AND REACTION VELOCITY DATA

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A method for the determination of the structure of dicarboxy compounds from their dissociation constants has been available for several years. Only quite recently, however, has data precise enough for a quantitative evaluation of the molecular dimensions of such compounds been secured. An application of the principles involved to the field of reaction velocity has yielded results in excellent accordance with values obtained from dissociation constants and x-ray studies.

An elementary statistical treatment of the two dissociation constants of a dicarboxylic acid shows that a simple, definite ratio should exist between the two constants for those special cases in which dissociation of the first H^+ ion does not interfere with dissociation of the second. In the more general case, interference effects arising from the electrical fields produced by the dissociated ions may be accounted for quantitatively by assuming a Boltzmann distribution of H^+. The further assumption of a Coulomb field of force between the charges on the ions gives an expression for the potential energy in the vicinity of an ion involving the "length" of the dicarboxylic ion under consideration. The "length" of the molecule thus introduced into the Boltzmann relation may be calculated from suitable and sufficiently precise experimental data.

This paper reviews the development of the method and summarizes its results. Section I presents the statistical treatment for special cases; Section II deals with the generalization of the method; Section III summarizes recent experimental results and Section IV describes the extension of the method to reaction velocity data.

## I. STATISTICAL TREATMENT OF DISSOCIATION CONSTANTS

James Walker (1) in 1892 compared his conductivity measurements of the first dissociation constant (K') of dicarboxylic acids with the dissociation constant (K_α) of the monoethyl ester of the corresponding acid as shown in table 1. He made the important observation that the ratio K'/K_α, given in the last column, lies between 2 and 2.5. Three years later, Wegscheider (2) demonstrated by statistical analysis that this ratio should be 2.

TABLE 1

Ratio of first dissociation constant of symmetrical acids to dissociation constant of corresponding monoethyl esters

ACID	FIRST DISSO-CIATION CON-STANT OF ACID K'	DISSOCIATION CONSTANT OF MONOETHYL ESTER K_α	RATIO K'/K_α
Malonic (s)	0.163	0.0451	3.6
Succinic (s)	0.0068	0.00302	2.3
Adipic (s)	0.00365	0.0025 (?)	·1.3
Suberic (s)	0.00296	0.00146	2.0
Sebacic (s)	0.00276	0.00143	1.9
Methylmalonic (s)	0.086	0.0387	2.2
Ethylmalonic (s)	0.127	0.0401	3.2
Dimethylmalonic (s)	0.076	0.0304	2.5
Diethylmalonic (s)	0.74	0.0231	32.0
Fumaric (s)	0.093	0.0473	2.0
Maleic (s)	1.17	0.110	10.6
Phthalic (s)	0.121	0.0551	2.2

Consider dicarboxylic acids of the type:

$$\text{HOOC}-\underset{\underset{H}{|}}{\overset{\overset{R_1}{|}}{C}}-(\text{CHR})_m-\underset{\underset{H}{|}}{\overset{\overset{R_2}{|}}{C}}-\text{COOH}$$
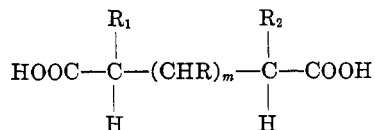
We shall call such an acid symmetrical when the radical R_1 is the same as R_2 and unsymmetrical if the radicals are different. For simplicity in representation we shall designate a symmetrical acid by the symbol HAAH, and unsymmetrical by HABH, the A and B portion of the symbol being introduced to label the particular H under consideration.

The first dissociation of an unsymmetrical dibasic acid may occur in two ways (figure 1), i.e., the H^+ at either end of the molecule may dissociate. The mass action constants for the two equilibria are:

$$K_1 = \frac{[H^+]\,[ABH^-]}{[HABH]}; \; K_2 = \frac{[HAB^-]\,[H^+]}{[HABH]} \tag{1}$$

Experimentally, we determine the first dissociation constant by measuring the equilibrium:

$$HABH \rightleftharpoons H^+ + ABH^- + HAB^- \tag{2}$$

or:
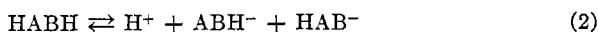
$$K' = \frac{[H^+]\,([ABH^-] + [HAB^-])}{[HABH]} \tag{3}$$

By addition it follows that:

$$K' = K_1 + K_2 \tag{4}$$

An unsymmetrical dibasic acid may have two isomeric mono-ethyl esters (HAB Et and Et ABH) depending on which carboxyl

HABH
K_1 K_2
$H^+ + ABH^-$ $HAB^- + H^+$

FIG. 1

HAB Et Et ABH
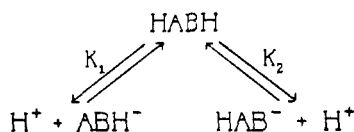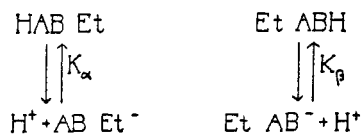K_α K_β
$H^+ + AB\;Et^-$ $Et\;AB^- + H^+$

FIG. 2

group is esterified; each of these may dissociate, resulting in the two equilibria represented in figure 2. Here:

$$K_\alpha = \frac{[H^+]\,[AB\;Et^-]}{[HAB\;Et]}; \; K_\beta = \frac{[Et\;AB^-]\,[H^+]}{[Et\;ABH]} \tag{5}$$

Now, if we make the assumption that a hydrogen at one end of a dicarboxylic acid molecule may dissociate uninfluenced by

the groups attached to the carboxyl group at the other end, we can say that[1]

$$K_1 = K_\alpha;\ K_2 = K_\beta \tag{6}$$

Therefore:

$$K' = K_\alpha + K_\beta \tag{6}$$

or the first dissociation constant of an unsymmetrical dicarboxylic acid is equal to the sum of the dissociation constants of the two isomeric monoethyl esters.

If the acid is symmetrical, $K_1 = K_2$ and, further, $K_\alpha = K_\beta$ since only one monoester is possible. Then:

$$K' = 2\,K_\alpha \quad \text{or} \quad K'/K_\alpha = 2 \tag{7}$$

which agrees with Walker's observation.

TABLE 2

Experimental and calculated first dissociation constants

ACID	K_α	K_β	K' FOUND	K' CALCULATED
Succinic (s)	0.00326	0.00326	0.0068	0.00652
Tartaric (s)	0.046	0.046	0.097	0.092
Phthalic (s)	0.0656	0.0656	0.121	0.1312
Camphoric (u)	0.000795	0.00108	0.00225	0.00188
Hemipic* (u)	0.016	0.130	0.145	0.146

* 3,4-dimethoxy-o-phthalic acid

The assumption of independently ionizable H^+ ions is not limited to ethyl esters; any monoesters should give like results. Table 2 shows the values of K_α, K_β, and K' found by Wegscheider for methyl esters of some symmetrical (s) and unsymmetrical (u) acids; the last column gives the values of K' calculated by the author through equations 6 and 7.

Chandler (3), in a study of the second dissociation constants of dibasic acids, found the ratio of the first dissociation constant (K') to the second (K'') approximately equal to 4 at certain con-

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[1] This follows since both K_1 and K_α are concerned with dissociation of H^+ at the A end of the molecule and we have assumed that the B end does not influence dissociation at A.

centrations. Adams (4), further developed Wegscheider's statistical treatment to demonstrate that the ratio K'/K'' should equal 4.

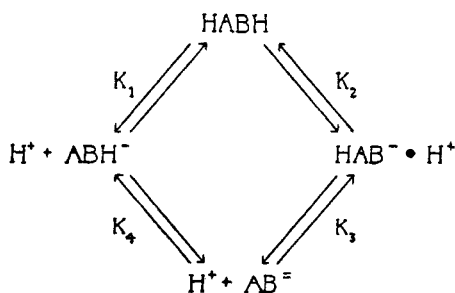Let us extend figure 1 to include the second dissociation of a dicarboxylic acid:

Fig. 3

The equations representing the added equilibria are given by:

$$K_3 = \frac{[H^+]\,[AB^=]}{[HAB^-]}; \quad K_4 = \frac{[H^+]\,[AB^=]}{[ABH^-]} \tag{8}$$

The experimentally determined second dissociation constant is represented by:

$$K'' = \frac{[H^+]\,[AB^=]}{[ABH^-] + [HAB^-]} \tag{9}$$

From equations 8 and 9:

$$K'' = \frac{1}{1/K_3 + 1/K_4} = \frac{K_3 K_4}{K_3 + K_4} \tag{10}$$

We shall now apply the general equations 4 and 10 to several types of dibasic acids.

Type I. A *symmetrical* acid with *independently* ionizable hydrogens.

Here, $K_1 = K_2 = K_3 = K_4 = K$

Equation 4 becomes $K' = 2K$ (4a)

Equation 10 becomes $K'' = K/2$ (10a)

and combining,

$$K'/K'' = 4 \qquad \text{(I)}$$

which is the ratio found by Chandler.

While it is easy in practice to satisfy the condition of symmetry in a dibasic acid, sufficient separation of the two acid groups to give independently ionizable hydrogens is far more difficult. In the triphenylmethane derivatives, however, both conditions are satisfied; for phenolphthalein (5), $K'/K'' = 4.06$ and for crystal violet (6), $K'/K'' = 4.08 \pm 5\%$.

Type II. An *unsymmetrical* acid with *independently* ionizable hydrogens.

In this case, $K_1 = K_3$ and $K_2 = K_4$, since the pair K_1 and K_3 is concerned with the same H^+ at one end of the molecule while K_2 and K_4 are both concerned with the H^+ at the opposite end. (Cf. footnote 1.)

$$\text{Equation 4 remains } K' = K_1 + K_2$$

$$\text{Equation 10 becomes } K'' = \frac{K_1 K_2}{K_1 + K_2} \qquad \text{(10b)}$$

Type III. *Symmetrical* and *unsymmetrical* acids; hydrogens do *not* ionize *independently.*

The majority of dibasic acids fall into this group. To obtain equations 4 and 10 for type III acids, we introduce the postulate suggested by the data that the negative charge arising in the molecule through dissociation of one H^+ diminishes the dissociation of the second hydrogen. Then:

$$K_3 < K_1 \text{ and } K_4 < K_2$$

$$\text{Equation 4 remains } K' = K_1 + K_2$$

$$\text{Equation 10 becomes}^2 K'' < \frac{K_1 K_2}{K_1 + K_2} \qquad \text{(10c)}$$

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[2] Equation 10 gives $K'' = \dfrac{1}{1/K_3 + 1/K_4}$. Since $K_3 < K_1$ and $K_4 < K_2$ then $\dfrac{1}{K_3}$ $> \dfrac{1}{K_1}$ and $\dfrac{1}{K_4} > \dfrac{1}{K_2}$. Substitution in equation 10 therefore shows $K'' <$ $\dfrac{1}{1/K_1 + 1/K_2}$ (10c).

and combining,[3]

$$K'/K'' > 4 \tag{II}$$

which is the general expression for symmetrical and unsymmetrical dibasic acids whose hydrogens are not independently ionizable. Table 3, taken in abbreviated form from Adams' paper, clearly shows that K'/K'' is greater than 4 in the general case.

II. GENERALIZED STATISTICAL TREATMENT OF DISSOCIATION CONSTANTS

A. Experimental relation of "n" and separation of carboxyl groups

Bjerrum (7) (1923) was the first to introduce a general quantitative treatment of dissociation constants. In accordance with

TABLE 3

Ratio of first to second dissociation constant for several dibasic acids

ACID	K'/K''	ACID	K'/K''
$(COOH)_2$	2,000	*cis* $C_2H_2(COOH)_2$	50,000
$(CH_2)(COOH)_2$	800	*trans* $C_2H_2(COOH)_2$	45
$(CH_2)_2(COOH)_2$	25	o-$C_6H_4(COOH)_2$	390
$(CH_2)_3(COOH)_2$	16.2	m-$C_6H_4(COOH)_2$	12
$(CH_2)_4(COOH)_2$	12.9	*cis* p-$C_6H_{10}(COOH)_2$	10
$(CH_2)_5(COOH)_2$	13.1	*trans* p-$C_6H_{10}(COOH)_2$	18
$(CH_2)_6(COOH)_2$	13.0	H_2SO_4	26
$(CH_2)_7(COOH)_2$	11.3	H_2SO_3	3,400
$(CH_2)_8(COOH)_2$	10.0	H_2CO_3	23,000

his terminology, we shall hereafter designate $-\log K'$ by p_1 and $-\log K''$ by p_2. As was shown in the preceding section, $K'/K'' =$

[3] From equations 4 and 10c, $\dfrac{K'}{K''} > \dfrac{(K_1 + K_2)^2}{K_1 K_2}$. For acids of type III, $K_1 \neq K_2$ or $K_1 - K_2 = a$ (or $K_2 - K_1 = a$), a being chosen positive. Then $\dfrac{(K_1 + K_2)^2}{K_1 K_2} = \dfrac{(2K_2 + a)^2}{K_2^2 + aK_2} = 4 + \dfrac{a^2}{K_2^2 + a}$. Since $\dfrac{a^2}{K_2^2 + a}$ is positive for type III unsymmetrical and zero for type III symmetrical acids, $K'/K'' > 4$. Acknowledgment is made to C. A. Marlies for suggesting this proof in place of the questionable method employed by Adams.

4 (I) for independent H^+ dissociation and $K'/K'' > 4$ (II) for the general case of dependent dissociation. Transposing to Bjerrum's units:

$$\text{Equation I becomes } p_2 - p_1 = \log 4 \qquad \text{(Ia)}$$

$$\text{Equation II becomes } p_2 - p_1 > \log 4 \qquad \text{(IIa)}$$

Now define a quantity, n, by the relation:

$$n \equiv p_2 - p_1 - \log 4 \qquad (11)$$

This n measures, in logarithmic units, the deviation of the ratio K'/K'' from the limiting value 4. When $K'/K'' = 4$, equation

TABLE 4

Dependence of n on separation, m, of carboxyl groups in the acids
$$HOOC—(CH_2)_m—COOH$$

ACID	m	p_1	p_2	$p_2 - p_1$	n
Oxalic	0	1.42	4.35	2.93	2.33
Malonic	1	2.80	5.69	2.89	2.29
Succinic	2	4.20	5.62	1.42	0.82
Glutaric	3	4.32	5.50	1.18	0.58
Pimelic	5	4.49	(5.36)?	(0.87)?	(0.27)?
Suberic	6	4.52	5.55	1.03	0.43
Azelaic	7	4.60	5.56	0.96	0.36
Sebacic	8	4.62	5.60	1.02	0.42

Ia holds and $n = 0$ (i.e., there is no deviation). The last column of table 4, taken from Bjerrum's paper, gives the values of n for the series of symmetrical acids: $HOOC—(CH_2)_m—COOH$.

It will be noticed that n decreases in value from 2.33 to 0.42 as the distance between the carboxyl groups increases (i.e., the deviation from the limiting ratio 4 becomes smaller, the greater the separation of the two dissociating groups). The fact that n is a function of the separation of the two carboxyl groups is further demonstrated in tables 5 and 6, where the separation of the carboxyl groups is kept constant although the nature of the acid is varied. Here n is practically a constant for a given type dibasic acid, even though the dissociation constants of the acids of that particular type vary over wide limits.

B. Quantitative relation between "n" and separation of carboxyl groups

At least two paths are open in a consideration of the influence of the first dissociation on the second:

1. Dissociation of a H+ from a COOH may produce intramolecular forces which, upon transmission through the molecule, may affect the second dissociation. At present, no simple physi-

TABLE 5

The constancy of n for a constant separation of carboxyl groups: glutaric acid types

Glutaric acid types—(COOH groups separated by 3 C)

ACID	p_1	p_2	$p_2 - p_1$	n
Glutaric	4.32	5.50	1.18	0.58
Thiodiglycolic*	3.31	4.46	1.15	0.55
Camphoric	4.65	5.8	1.15	0.55
m-Phthalic	3.54	4.60	1.06	0.46

* Separation of COOH groups by 2 C and 1 S.

TABLE 6

The constancy of n for a constant separation of carboxyl groups: succinic acid types

Succinic acid types—(COOH groups separated by 2 C)

ACID	p_1	p_2	$p_2 - p_1$	n
Succinic	4.20	5.62	1.42	0.82
d-Tartaric	3.02	4.39	1.37	0.77
Dibromosuccinic	1.47	2.80	1.33	0.73
Fumaric	3.03	4.47	1.44	0.84
o-Phthalic	2.92	5.45	2.53	1.93
Maleic	1.93	6.29	4.36	3.76

cal picture of intramolecular forces is available for a calculation of such effects; we must rely upon experiment.

2. The negative COO⁻ arising from dissociation of a H+ may attract H+ to itself. The resultant local accumulation of H+ around the COO⁻ over and above the average distribution of H+ throughout the solution may influence the second dissociation. Such an electrostatic effect is amenable to a simple mathematical treatment.

A consideration of the most probable arrangement of a system of particles subject to the conditions that the total number of particles and their *total* energy remain constant, although the energy distribution among the particles may vary, leads to the Maxwell-Boltzmann distribution law (8) for such partition of energy among the particles:

$$C = C_0 \exp.^{\frac{\phi}{RT/N}} \tag{12}$$

where C = the concentration at any point,

C_0 = the average concentration throughout the system,

ϕ = the work necessary to bring a molecule from a point at concentration C to a point at concentration C_0,
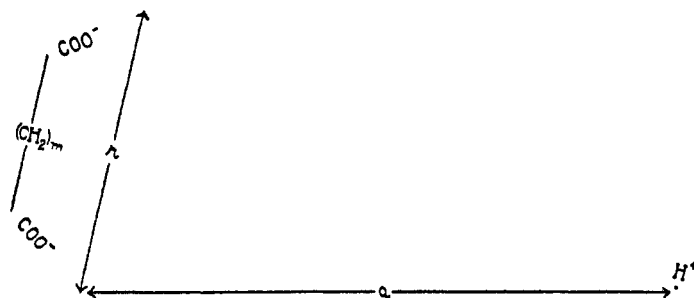

FIG. 4

R = the gas constant,

T = the absolute temperature, and

N = the Avogadro number.

The electrical work necessary to separate a positive H^+ from a negative COO^- by a distance "a" (figure 4) is given (9) by

$$\phi = \frac{e^2}{Da} \tag{13}$$

where e = the elementary charge, and

D = the dielectric constant of the medium.

Application of the Maxwell-Boltzmann law to the distribution of positive charges (H^+) in the neighborhood of a negative charge (COO^-) yields:

$$C_a = C_0 \exp.^{\frac{e^2 N}{DRT \cdot a}} \tag{14}$$

where C_a = the concentration of H^+ at distance "a." Physically, this tells us that the concentration of H^+ in the immediate vicinity of a negative COO^- is greater than the average H^+ concentration throughout the solution by an exponential factor involving the distance from the COO^- group. The closer we approach COO^-, the greater the concentration of H^+.

If we designate by "r" the distance between the charges on the doubly charged ^-OOC—$(CH_2)_m$—COO^- ion, or between corresponding points in the monovalent ion or uncharged molecule, equation 14 becomes:

$$C_r = C_0 \exp.^{\frac{e^2N}{DRT \cdot r}} \tag{14a}$$

The accumulation of H^+ near the second carboxyl group due to the charge on the first COO^- group might interfere with dissociation of the second H^+. With no interference, $K'/K'' = 4$ (I); in general, however, $K'/K'' > 4$ or $n > 0$. If we assume that deviation of the ratio K'/K'' from 4 arises entirely from electrostatic effects (i.e., due to the Boltzman exponential factor), then the experimentally determined logarithmic deviation n and the mathematically calculated deviation factor $\exp.^{\frac{e^2N}{DRT \cdot r}}$ may be equated:

$$n = \log_{10} \exp.^{\frac{e^2N}{DRT \cdot r}} \tag{III}$$

or

$$K'/K'' = 4 \exp.^{\frac{e^2N}{DRT \cdot r}} \tag{IV}$$

Thus, we have succeeded in relating an experimental value (K'/K'' or n) with "r," the "effective length" of a dicarboxylic acid molecule. Substitution of the values

$$e = 4.77 \times 10^{-10} \text{ E.S.U.}$$

$$N = 6.06 \times 10^{23}$$

$$D = 80 \text{ for } H_2O$$

$$R = 8.35 \times 10^7$$

$$T = 293$$

gives

$$n = \frac{3.1}{r \times 10^8} \qquad (15)$$

In table 7 the values of r calculated by means of equation 15 for the acids of table 4 are shown. The separation of centers of K^+ and Cl^- in the KCl crystal is 3.14 Å. (10a) and between C—C in the diamond 1.54 Å., so that the values of r calculated above are of the correct order of magnitude.

Simms (24a) applied these calculations in an attempt to evaluate the "distortional" effects of H^+ ion dissociation. Bjerrum (7), Simms (24b), and Hückel (25) made further calculations on this basis, e.g., comparing "r" for *cis-trans* isomers and evaluating

TABLE 7

The length of some dicarboxy molecules calculated from the logarithmic deviation

ACID	m	n (table 4)	r
			Å.
Oxalic	0	2.33	1.33
Malonic	1	2.29	1.35
Succinic	2	0.82	3.8
Glutaric	3	0.58	5.3
Others	6–8	0.40	7.8

inorganic dibasic acid distances, but more precise experimental data was necessary for significant results.

III. RECENT EXPERIMENTAL RESULTS

Gane and Ingold (11) undertook an extensive and precise experimental investigation of dicarboxylic acid dissociation constants to test the applicability of Bjerrum's calculations. Previous determinations had usually been made by different methods, e.g., K' by conductivity, K'' by partition or sugar inversion experiments. A method that permitted measurement of both K' and K'' by the same experimental procedure at the same time and under the same environmental conditions was essential for obtaining suitable data. In 1924, such a method had been made available by Auerbach and Smolczyk (12).

The procedure consisted of adding small portions of sodium hydroxide to a solution of the dibasic acid and determining the pH electrometrically after each addition of alkali. Then, if

C, v = initial concentration and volume of acid,

N, x = concentration and volume of alkali after the addition of which the hydrogen ion concentration = [H$^+$],

K', K'', K_w = the first and second dissociation constants for the acid and the water constant, respectively,

[Na$^+$] = the concentration of sodium ion in solution, and

[H$_2$A],[HA$^-$], [A$^-$] = the concentration of undissociated acid, monovalent, and divalent ions, respectively,

the following six equations can be set up, assuming complete dissociation of the base added and salts formed and restricting the calculation to weak acids.

$$[H^+] = K' \frac{[H_2A]}{[HA^-]}$$
$$\left. \right\} \text{Mass action expressions for weak acids}$$
(16)

$$[H^+] = K'' \frac{[HA^-]}{[A^-]}$$
(17)

$$[Na^+] + [H^+] = [HA^-] + 2[A^-] \text{ Electrical neutrality}$$
(18)

$$[H_2A] + [HA^-] + [A^-] = \frac{Cv}{v + x}$$
(19)

$$[Na^+] = \frac{nx}{v + x}$$
(20)

$$[H^+] \times [OH^-] = K_w$$
(21)

A solution of these simultaneous conditional equations results in the expression:

$$\frac{x}{v} = \frac{K'C \, ([H^+]^2 + 2K''[H^+]) - ([H^+]^2 - K_w) \, ([H^+]^2 + K' \, [H^+] + K'K'')}{([H^+]^2 + K'[H^+] + K'K'') \, ([H^+]^2 + N[H^+] - K_w)}$$
(22)

This equation contains only two unknowns, K' and K''. Therefore, any two pH measurements during titration suffice to solve

the expression for the two unknowns; the series of pH values actually determined gives a precise average value for K' and K''.

To fulfill the condition of complete dissociation of alkali and salts, dilute solutions (approximately 0.06 to 0.0007 M) were used by Gane and Ingold; further, calculations for oxalic acid by this

TABLE 8

More precise values of the length for the series HOOC—(CH₂)$_m$—COOH

ACID	m	$K' \times 10^5$	$k'' \times 10^4$	r
				Å.
Oxalic	0	......	....	....
Malonic	1	177.0	4.37	1.5
Succinic	2	7.36	4.50	5.0
Glutaric	3	4.60	5.34	9.2
Adipic	4	3.90	5.29	11.5
Pimelic	5	3.33	4.87	13.2
Suberic	6	3.07	4.71	14.5
Azelaic	7	2.82	4.64	16.8

TABLE 9

Effect of substitution of radicals on length of dicarboxylic acid molecule

ACID	$K' \times 10^5$	$K'' \times 10^8$	r
			Å.
Glutaric	4.60	534	9.22
Substituted glutaric acids			
β-Methyl	5.77	62.8	2.27
β-n-Propyl	4.97	43.2	2.12
β,β-Dimethyl	20.3	55.1	1.57
β,β-Diethyl	30.4	7.85	1.02
β,β-Di-n-propyl	20.3	5.42	1.01
Cyclo acids			
Cyclopentane-1,1-diacetic	16.8	26.3	1.40
Cyclohexane-1,1-diacetic	33.6	10.2	1.04
Cycloheptane-1,1-diacetic	27.8	10.9	1.10

method were excluded because K' does not follow the mass action law. Table 8 summarizes the K' and K'' values determined by this method for the series HOOC—(CH₂)$_m$—COOH, and the "r" values calculated from Bjerrum's equation (IV).

An empirical expression satisfactory for the last five acids,

$r = 4.4 + 1.73\, m$, assigns a value of 1.73 Å. increase per additional CH_2 group and points to a straight or zigzag chain rather than a coiled structure for these aliphatic acids. The deviations exhibited by the first two may be attributed to internal polar effects which increase with shortening of the chain.

The structure of several substituted dicarboxylic acids was next determined by this method (13). A short summary of results is given by table 9.

In the case of unsubstituted glutaric acid, $r = 9.22$ Å., whereas substitution of one methyl or propyl on the central carbon reduces the distance between the carboxyl groups to about 2 Å.; substitution of two radicals cuts the distance to 1 Å. Apparently, substitution on the central carbon tends to coil the long chain acid, thereby bringing the carboxyl groups closer (figures 5a, 5b).
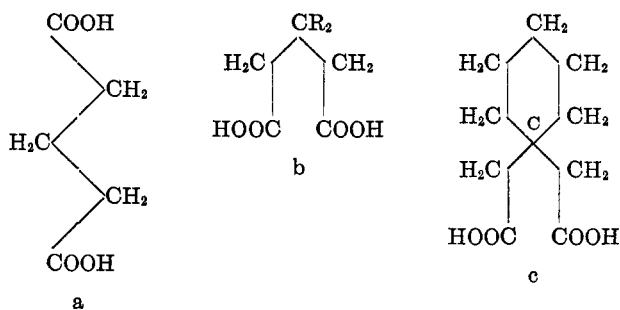

FIG. 5

The r values for cyclic (figure 5c) 1,1-diacetic acids (table 9) are in harmony with the coiled structure (figure 5b) assigned to substituted glutaric acids. This structure is in further accord with much chemical evidence and is believed by Ingold to support the valency deflection hypothesis (14).

Among the most serious disturbances to calculations of this type are effects caused by polar transmission through the molecule and by local variations in the properties of the medium. Internal transmission effects may be disregarded when the carboxyl groups are separated by more than two carbon atoms (cf. table 8).

Solvent disturbances were studied by Gane and Ingold in a fourth paper (15). Correction for interionic effects were made by

titrating each dibasic acid at several concentrations in the very dilute region and extrapolating to $\mu = 0$.[4] Table 10 shows an example of this type of correction.

Corrections for solvent effects caused by compressibility of the solvent in the neighborhood of an ion, by anisotropy (electrical and optical) and by association are treated in Ingold's "Remarks on the Electrical and Mechanical Conditions in the Neighborhood of a Dissolved Ion" (16).   A method of approximations yields an

TABLE 10

Corrections for interionic effects

ACID	10^3C	$10^4K'$	$10^7K''$
Malonic...................	5.000	17.7	41.2
	4.991	17.7	43.7
	2.000	15.8	25.5
	1.000	15.3	24.3
	1.000	15.4	23.8
	0.400	15.1	21.1
	0.125	14.9	21.2
	$\mu = 0$	14.9	20.3
Succinic...................	5.000	0.734	46.1
	4.880	0.736	45.0
	2.000	0.678	37.8
	1.000	0.659	36.6
	0.400	0.648	35.0
	0.125	0.644	33.5
	$\mu = 0$	0.641	33.3

expression for the potential, ψ, in the vicinity of an ion corrected for the above factors, taking the form of a series in terms of

$$ e\left[\frac{a'e}{r} + \frac{a''e^3}{r^5} + \ldots\ldots\ldots\ldots\right] $$

instead of the simplified form used by Bjerrum (equation 13).

Another question examined is that of the flexibility of the molecule (15).   An equation for K'/K'' was derived for flexible mole-

[4] μ = ionic strength = $\Sigma \frac{1}{2}$ molar concentration $\times$ (valence of ion)^2.

cules on the assumption that a definite maximum, r_{max}, and a definite minimum, r_{min}, separation exists between the carboxyl groups. The distribution of undissociated molecules and monovalent ions is such that there are as many of these with length, r_1, as with length, r_2, within the limits set by r_{max} and r_{min}. In the case of the divalent ions, however, there are more (Boltzmann distribution) with larger r's than with smaller lengths since the repulsion of the like charges at each end of the divalent ion tends to stretch it. Since the energy necessary to stretch the molecules to the lengths calculated on this basis is very great, it is concluded

TABLE 11

Length of dicarboxy molecules calculated from corrected dissociation data and from assumed zigzag chain model

ACID	m	r_{obs}	r_{calc}	Δr
		$\overset{\circ}{A}.$	$\overset{\circ}{A}.$	$\overset{\circ}{A}.$
Oxalic	0	(3.37)	(3.54)	(−0.17)
Malonic	1	3.43	4.26	−0.83
Succinic	2	5.58	5.87	−0.29
Glutaric	3	7.11	6.84	+0.27
Adipic	4	8.22	8.36	−0.14
Pimelic	5	9.43	9.43	0.00
Suberic	6	11.07	10.88	+0.19
Azelaic	7	12.03	12.04	−0.01

that the dicarboxy molecule has a rigid structure. Thus, Gane and Ingold propose that a major portion of the force tending to maintain a favored configuration in crystals, liquids, and dilute solutions is intramolecular and not externally electrostatic in origin.

The column (r_{obs} Å.) of table 11 was calculated after applying all the above noted corrections. Its values may be expressed by the linear equation, $r = 2.98 + 1.29\ m$ Å., indicating an increase of 1.29 Å. per CH_2 group, a value well in accord with x-ray data (10c, 17).

When $m = 0$, $r = 2.98$, a measure of the distance between the charges in two COO^- groups. The distance between the charge on the COO^- and the carbon of this group measured along the

line connecting the two carbons in the molecule (figure 6) is calculated to be 1.00 Å. Using this result together with a zigzag model for the dicarboxylic acids and the appropriate trigonometrical relations, column 4 of table 11 was obtained. The last column shows deviations between values calculated from observational data and from the zigzag model. The good agreement points to a rigidly extended zigzag configuration for dicarboxylic acids in dilute aqueous solutions.
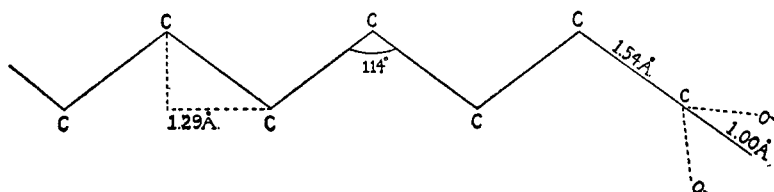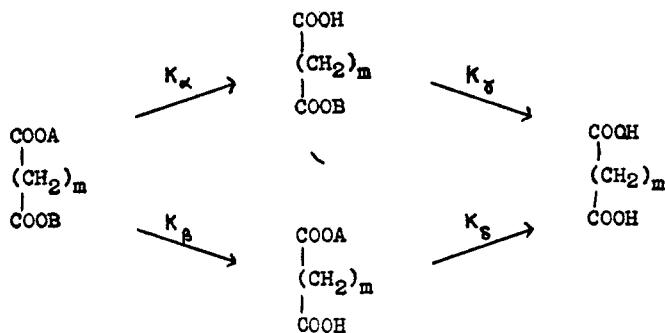

FIG. 6

FIG. 7

IV. APPLICATION TO REACTION VELOCITY DATA

A general formula relating to the several velocity constants of hydrolysis of a polyester was statistically derived by Ingold (18) assuming no interaction of the ester groups. The present author submits the following simplified derivation to illustrate the method for the hydrolysis of a diester.

Let k_α, k_β, k_γ, k_δ, and v_α, v_β, v_γ, v_δ, be the specific velocity con-

stants and the velocities of acid hydrolysis of the corresponding stepwise reactions represented in figure 7. Then,

$$k_\alpha = \frac{v_\alpha}{[AB]}; \; k_\beta = \frac{v_\beta}{[AB]}; \; k_\gamma \frac{v_\gamma}{[BH]}; \; k_\delta = \frac{v_\delta}{[AH]} \qquad (22)$$

If k_1 and k_2 are the experimentally determined first and second hydrolysis constants of the diester, and v_1 and v_2 the experimentally measured velocities, then:

$$v_1 = k_1[AB] = v_\alpha + v_\beta = (k_\alpha + k_\beta) \, [AB] \qquad (23)$$

or

$$k_1 = k_\alpha + k_\beta \qquad (24)$$

and

$$v_2 = k_2 \, ([AH] + [BH]) = v_\gamma + v_\delta \qquad (25)$$

But

$$[AH] + [BH] = \frac{v_\gamma}{k_\gamma} + \frac{v_\delta}{k_\delta} \qquad (26)$$

therefore

$$k_2 \left[\frac{v_\gamma}{k_\gamma} + \frac{v_\delta}{k_\delta} \right] = v_\gamma + v_\delta \qquad (27)$$

For a symmetrical ester $(A = B)$ with independent hydrolysis at each end of the chain,

$$k_\alpha = k_\beta = k_\gamma = k_\delta = k$$

and

$$\text{Equation 24 becomes } k_1 = 2 \, k \qquad (24a)$$

$$\text{Equation 27 becomes } k_2 = k \qquad (27a)$$

or, combining,

$$k_1/k_2 = 2 \qquad (28)$$

Thus, the ratio of the first to the second velocity constants of hydrolysis should be 2 for a symmetrical ester without inter-

action of the two ester groups. Table 12 abbreviated from Ingold (18) shows experimental values for the acid hydrolysis of some symmetrical esters; the k_1/k_2 ratio found is closely equal to 2.

TABLE 12

*Experimental and calculated ratio of first to second velocity of acid hydrolysis constants for some diesters*

ESTER	$k_1 \times 10^3$	$k_2 \times 10^5$	k_1/k_2 FOUND	k_1/k_2 CALCULATED
Dimethyl succinate	2.40	121	1.98	2.00
Diethyl succinate	2.30	121	1.90	2.00
Dimethyl d-tartrate	1.24	62	2.00	2.00
Diethyl d-tartrate	1.40	68	2.06	2.00

TABLE 13

Length of dicarboxy molecules calculated from velocity constant and from dissociation constant ratios

| ESTER	k_1/k_2	MEAN k_1/k_2	MEAN r FROM VELOCITY DATA	r FROM DISSOCIATION DATA
Dimethyl oxalate	(10^4)	(10^4)	(2.9)	(3.37)
Diethyl oxalate	(10^4)			
Dimethyl malonate	(92)	(91)	(3.8)	3.43
Diethyl malonate	(90)			
Dimethyl succinate	9.66	9.64	5.62	5.58
Diethyl succinate	9.62			
Dimethyl glutarate	6.45	6.42	6.83	7.11
Diethyl glutarate	6.40			
Dimethyl adipate	4.95	4.97	8.30	8.22
Diethyl adipate	5.00			
Dimethyl pimelate	4.34	4.34	9.57	9.43
Dimethyl suberate	3.91	3.91	10.97	11.07
Dimethyl azelate	3.61	3.61	12.38	12.03

This limiting ratio of 2 is found not to hold for the alkaline hydrolysis of diesters, nor would we, in the light of the Brönsted theory of reaction velocity (19, 20a), expect the preceding simple assumptions to hold. We are dealing with charged ions in the second stage of alkaline hydrolysis.

The first step of the reaction between the diester and the OH$^-$ ion may be represented by the formation of the intermediate complex:

$$ROOC—(CH_2)_m—COOR + OH^- \rightarrow ROOC—(CH_2)_m—COOR \cdot OH^-$$
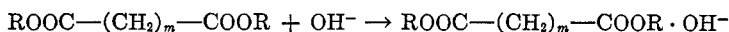
with reaction taking place between an uncharged molecule and a negative ion.

In the second stage, however, the following reaction between two like charged ions will occur:

$$ROOC—(CH_2)_m—COO^- + OH^- \rightarrow HO^- \cdot ROOC—(CH_2)_m—COO^-$$
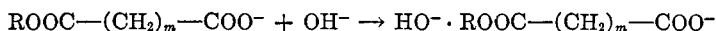
The presence of a charged COO$^-$ group will cause a decrease of like charged OH$^-$ ions in the immediate vicinity of COO$^-$. Consequently, there will be a decrease in the number of critical complexes below the number that would form in the absence of charge effects.

We would not expect k_1/k_2 to equal 2 for alkaline hydrolysis, but

$$k_1/k_2 = 2 \exp.^{\frac{\phi}{kT}} \tag{29}$$

where the Boltzmann exponential factor once again takes care of electrostatic influences. The potential term, ϕ, here too involves the distance, "r," between the charges on the COO$^-$ groups (assuming the OH$^-$ to form a critical complex at the carboxyl group).

By employing the modified expression for ϕ (16) and working in dilute solutions to correct for interionic effects, Ingold (21) obtained the following values of k_1/k_2 (table 13) for the alkaline hydrolysis of some diesters. The "r" values were determined by means of equation 29. The last column, giving r values calculated from the dissociation constant ratio (table 11), shows excellent agreement and indicates a zigzag model for both dicarboxy esters and dicarboxylic acids.

It must be emphasized that this method is by no means restricted to dicarboxy compounds but provides a perfectly general way of calculating molecular dimensions from the proper data. La Mer (20b) has made a similar calculation for the thiosulfate-

bromoacetate ion and ester reaction and secured a very reasonable "length" for the bromoacetate molecule.

At the date of writing this review, an attempt by Eucken (22) to use this method for calculating various molecular properties (e.g., internal dielectric constant of a molecule) of a series of substituted organic acids has appeared. MacInnes (23) has obtained an interesting relationship for a group of substituted monocarboxylic acids which is in harmony with calculations of the Bjerrum type.

These recent applications serve to emphasize the generality and utility of this method of attack on molecular properties in solution; many interesting results may be awaited from similar calculations.

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