the hydrochloride of 2,4,6-tribromoaniline. It was recrystallized three times from alcohol (thereby of course losing its added molecule of hydrochloric acid) and then melted at 119°, and showed the other properties of 2,4,6-tribromoaniline.

Calculated for $C_6H_4NBr_3$: Br, 72.71; found, 73.11.

The action of bromine was tried on 3,5-dibromo-4-aminobenzophenone in certain preliminary studies which will be continued. No splitting apart of the two benzene nuclei takes place as with the corresponding hydrol, but perbromide bodies are formed.

This research will be continued in this laboratory and extended to other benzhydrol derivatives.

CAMBRIDGE, MASS.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY. NO. 69.]

THE ELECTRON CONCEPTION OF VALENCE. II. THE ORGANIC ACIDS.

BY K. GEORGE FALK.

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1. Introduction. 2. Theoretical Considerations. 3. Saturated Monobasic Acids. 4. Saturated Dibasic Acids. 5. Unsaturated Acids. 6. Aromatic Acids. 7. Summary.

1. Introduction.—The hypothesis of Sir J. J. Thomson, according to which the linkages or bonds between the atoms in a molecule are formed by the transfer of corpuscles, was developed mainly in relation to organic compounds in a preceding article.[1] It will be applied in this paper to the ionization relations of organic acids. The ionization constants ($K \times 10^5$) of the acids as calculated from the Ostwald dilution law, $K = \frac{\gamma^2}{v(1-\gamma)}$, in which v = the volume in cubic centimeters containing one mol of the acid, and γ = the degree of ionization found from the conductance ratio, will be used. The factors upon which the accuracy and reliability of K depend for any one acid at a definit temperature for a series of concentrations have been discussed in detail by Scudder.[2] Only those acids will be considered for which a fairly reliable value of K has been obtained. This eliminates the highly ionized acids for which K varies with change in concentration. The data refer to 25° and the results of a number of different observers have been used.[3]

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[1] Falk and Nelson, THIS JOURNAL, 32, 1637–54 (1910).

[2] *J. Physic. Chem.*, 7, 293 (1903).

[3] Ostwald, *Z. physik. Chem.*, 3, 170, 241, 369 (1889). Bethman, *Ibid.*, 5, 385 (1890). Berthelot, *Ann. chim. phys.*, [6], 23, 43 (1891). Crum Brown and Walker, *Ann.*, 261, 116 (1891). Walker, *J. Chem. Soc.*, 61, 696 (1892). Walden, *Z. physik. Chem.*, 8, 448 (1891); 10, 646 (1892). Stohmann and Kleber, *J. prakt. Chem.*, 45, 480

2. Theoretical Considerations.—The principles upon which the directions of the valences are assumed to depend were explained in the first paper. It may suffice to state here that for a single bond the corpuscle for the carbon-hydrogen union is assumed to pass from the hydrogen to the carbon, the former becoming positively charged, the latter negatively, while for the carbon-chlorine union, the corpuscle passes from the carbon to the chlorine. For a double or triple bond there are more possibilities of union between two atoms, but in general, one of the cases involving certain definit valence directions will represent the most stable form of the compound in question. The arrangement of the elements in the periodic system serves in general to indicate the electrical relations of the elements to each other in the production of a bond.

In considering the structures of the organic acids, it is evident that the α-carbon atom (the one combined directly with the carboxyl group) influences the ionization constant of the acid to the greatest extent. A classification of the acids will be given here, which depends upon the direction of the valences by which this α-carbon atom is combined with the other atoms in the molecule. This divides the acids into four general classes, which may be formulated as follows:

I. $\begin{smallmatrix}\rightarrow\\ \rightarrow\\ \rightarrow\end{smallmatrix}C.CO_2H$; II. $\begin{smallmatrix}\leftarrow\\ \rightarrow\\ \rightarrow\end{smallmatrix}C.CO_2H$; III. $\begin{smallmatrix}\leftarrow\\ \leftarrow\\ \rightarrow\end{smallmatrix}C.CO_2H$; IV. $\begin{smallmatrix}\leftarrow\\ \leftarrow\\ \leftarrow\end{smallmatrix}C.CO_2H$.

The acids belonging to class I are those in which three electropositive groups are combined with the α-carbon atom; those belonging to class II, two electropositive and one electronegative; to class III, one electropositive and two electronegative. The ionization constants are found to increase in the order of the classes I, II, III, IV. The acids represented by formula IV, such as trichloroacetic acid, are too highly ionized to give satisfactory dissociation constants, and will not be considered in detail here.

This method of consideration differs from the ordinary one, which attributes the variations of the ionization constant directly to the nature of the neighboring atoms or groups, in assuming that the influences determining the magnitude of the ionization constant are the positions of the electric charges or corpuscles. These positions indeed are determined by the nature of the adjacent atoms or groups, so that the new hypothesis is to be regarded as a development of the older idea, which serves to give it greater definitness. The "direction of the bonds or valences" and the arrows representing this direction are merely a convenient conven-

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(1892). Hantzsch and Miolati, *Z. physik. Chem.*, **10**, 23 (1892). Franke, *Ibid.*, **16**, 482 (1895). Euler, *Ibid.*, **21**, 264 (1896). Szyszkowski, *Ibid.*, **22**, 173 (1897). Smith, *Ibid.*, **25**, 194 (1898). Bone and Sprankling, *J. Chem. Soc.*, **77**, 673 (1900). Lichty, *Ann.*, **319**, 380 (1901). Bone, Sudborough and Sprankling, *J. Chem. Soc.*, **85**, 540 (1904). Drucker, *Z. physik. Chem.*, **52**, 642 (1905).

tional method of expressing the location of the negative charge, which is always to be considered as located at the point of the arrow.

The influences exerted by the double or triple bond, according to the new point of view, are made up additively of the influences exerted by the two or three single bonds or valences. Thus, the ionization constant for maleic acid, having the formula[1] $HO_2C.CH \rightrightarrows CH.CO_2H$, depends mainly upon the identical directions of the valences making up the double bond, and that of fumaric acid, whose formula[1] is $HO_2C.CH \rightleftarrows CH.CO_2H$, differs from that of maleic acid since the directions of the valences of the double bond of the α-carbon atom lie in opposit directions.

The groups combined with the β-carbon atom, or the directions of the valences of this atom, doubtless influence the ionization constant; but as will be seen, this influence is in most case of small importance when compared with the influence exerted by the bonds of the α-carbon atom, and while the acids substituted in the β-position may have ionization constants lying between those for class I and class II, for example, there should be no doubt in most cases as to the class to which the acid should be assigned. The groups combined in the γ, δ, etc., positions doubtless exert an influence on the constants also, but this influence is negligible in the consideration of this classification.

Although the classification just given depends primarily upon the directions of the valences, the specific effect of certain groupings may be great enough at times to exert a predominating influence and obscure the relations just described. These effects, which are unquestionably present with every atom or group in an acid, are too small to be perceived with the present methods of experiment and calculation and therefore do not interfere when the acids are divided into the general classes depending on the directions of the valences of the α-carbon atom except, possibly, in individual cases.

Acids which contain an amino group will not be included in the discussion, and all acids containing sulfur have been omitted as well.

3. *Saturated Monobasic Acids.*—In the aliphatic acids containing only carbon and hydrogen in combination with the carboxyl group, the arrangement of the bonds of the α-carbon atom (that combined directly with the carboxyl group) may, as stated, be represented by the formula $\begin{matrix}\rightarrow\\ \rightarrow\\ \rightarrow\end{matrix} C—CO_2H$, in which the direction of the heads of the arrows representing the bonds indicate the direction of the transfer of the negative corpuscles. The values of the constant ($K \times 10^5$) for these acids vary between 0.0011 and 0.0020 and include the following, arranged in the order of increasing values for the constant: pelargonic, caprylic, caproic, isobutyric, heptylic, isocaproic, butyric, valeric, ethylmethylacetic, iso-

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[1] *Loc. cit.*, p. 1643.

valeric, acetic, tetramethylenecarboxylic, and diethylacetic. The following acids and their dissociation constants contain the same bonds for the α-carbon atom as the acids just considered, but are substituted by halogens, hydroxyl groups, phenyl groups, etc., in the β-, γ-, or δ-positions: δ-chlorovaleric, 0.0020; benzoylpropionic, 0.0022; hydrocinnamic, 0.0023; levulinic, 0.0026; β-hydroxypropionic, 0.0031; β-chloropropionic, 0.0086; β-chlorobutyric, 0.0089; β-iodobutyric, 0.0090; β-bromopropionic, 0.0098; and eleven substituted β-hydroxypropionic acids,[1] 0.0015 to 0.0045. To these may be added phenylacetic, 0.0056, and hydroatropic, 0.0043, indicating that the phenyl group as a substituent exerts an influence on the ionization constants of acids similar to that exerted by the methyl, etc., groups.[2] The ionization constants for these acids are less than 0.005 except for the three β-halogen propionic and phenylacetic acids, and for these they are less than 0.01. The constitutive effect is evident here, but it is not great enough to mask the additive influence of the bonds (as will be seen presently with the *a*-halogen substituted acids). For the acids containing the grouping $\begin{smallmatrix}\rightarrow\\ \rightarrow\\ \rightarrow\end{smallmatrix}\mathrm{C{—}CO_2H}$, the constant may be taken in general to lie between 0.001 and 0.005 with variations due to the constitutive effect of the substituting groups up to 0.01 and perhaps higher.[3]

The formula for the aliphatic acids containing a halogen or similar (negative) substituent in the α-position may be represented by $\begin{smallmatrix}\leftarrow\\ \rightarrow\\ \rightarrow\end{smallmatrix}\mathrm{C{—}CO_2H}$. The acids belonging to this class which have been studied are iodoacetic, 0.075; α-bromobutyric, 0.106; α-bromopropionic, 0.108; bromoacetic, 0.138; α-chlorobutyric, 0.139; α-chloropropionic, 0.147; chloroacetic, 0.155; sulfocyanoacetic, 0.265; cyanoacetic, 0.370; and α,β-dibromopropionic, 0.67.[4] For acids of this class, the constant may be taken as lying between 0.1 and 0.4 unless modified very markedly by some constitutive influence.

Few acids containing two negative substituents in the α-position of the formula $\begin{smallmatrix}\leftarrow\\ \leftarrow\\ \rightarrow\end{smallmatrix}\mathrm{C{—}CO_2H}$ have been studied. α,α-Dibromopropionic, 3.3, and dichloroacetic, 5.2, are the only ones for which data were found. Acids containing three negative constituents in the α-position are too highly ionized for the purpose in view and do not give a satisfactory constant.

The constants for the acids so far considered may be summarized as follows: For the grouping $\begin{smallmatrix}\rightarrow\\ \rightarrow\\ \rightarrow\end{smallmatrix}\mathrm{C{—}CO_2H}$, less than 0.01; for $\begin{smallmatrix}\leftarrow\\ \rightarrow\\ \rightarrow\end{smallmatrix}\mathrm{C{—}}$

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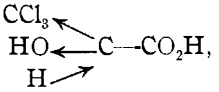
[1] Szyszkowski, *Loc. cit.*

[2] This coincides with the view advocated by Michael and Leighton as to the comparative influence of the phenyl and methyl groups. *Ber.*, 39, 2792 (1906).

[3] Whether a β,β-dihalogen propionic acid would have a larger constant is a question which can be answered only by experiment.

[4] For the dilutions between 32 and 128 liters.

CO_2H, 0.1–0.4; for $\substack{\longleftarrow \\ \longleftarrow \\ \longrightarrow}$ $C—CO_2H$, greater than 2. Individual substituents modify these values to a greater or less extent, but the differences between the three classes appear to be great enough to enable a decision to be reached as to the structure of a given acid in most cases.

A group of acids for which the constants lie between those for the acids containing the groupings $\substack{\longrightarrow \\ \longrightarrow \\ \longrightarrow}$ $C—CO_2H$ and $\substack{\longleftarrow \\ \longrightarrow \\ \longrightarrow}$ $C—CO_2H$ is known. This group comprizes the acids diisopropylglycolic, 0.013; lactic, 0.014; glycolic, 0.015; glyceric, 0.023; ethoxyacetic, 0.023; methoxyacetic, 0.034; mandelic, 0.042; phenoxyacetic, 0.076; and benzilic, 0.092. The OR (R = H or hydrocarbon radical) group is evidently the reason why these acids occupy an intermediate position between the acids containing no negative α-group and those containing one. This OR group is generally taken to have an effect similar to a negative group, and would therefore be formulated $\longrightarrow OR$ in the acids Some of the acids approach the values for acids of the class $\substack{\longleftarrow \\ \longrightarrow \\ \longrightarrow}$ $C—CO_2H$, but for most of them the difference is so large that it must be assumed that either the OR group exerts a constitutive influence masking to a great extent the effect of the bonds or that there is some action[1] between the ether or hydroxyl oxygen and the hydrogen or other part of the carboxyl group which decreases the values of K for this group of acids as compared with the acids containing a different negative substituent in the α-position, resulting in a constant of from 0.01 to 0.1. It may be pointed out, however, that the class to which any given acid belongs may readily be ascertained as the composition taken in connection with the dissociation constant shows the structure of the α-carbon atom. An acid such as trichlorolactic, 0.465, must be formulated somewhat differently and probably is best represented by the structure  $\begin{array}{l} CCl_3 \nwarrow \\ HO \longleftarrow C—CO_2H \\ H \nearrow \end{array}$, or intermediate between the $\substack{\longleftarrow \\ \longrightarrow \\ \longrightarrow}$ $C—CO_2H$ and $\substack{\longleftarrow \\ \longleftarrow \\ \longrightarrow}$ $C—CO_2H$ classes, just as lactic acid is intermediate between the $\substack{\longrightarrow \\ \longrightarrow \\ \longrightarrow}$ $C—CO_2H$ and $\substack{\longleftarrow \\ \longrightarrow \\ \longrightarrow}$ $C—CO_2H$ classes.

4. *Saturated Dibasic Acids.*—Ostwald was the first to point out that the constants obtained by his dilution law for the organic dibasic acids referred to the first hydrogen ion which was formed from the acid and that the second hydrogen ionizes only in very dilute solutions, so that it does not enter into the constant as ordinarily determined. For some acids the second hydrogen begins to ionize appreciably at a dilution of about 500 liters, but the constant as determined experimentally in the usual way is found to increase rapidly with the dilution when this oc-

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[1] Such as inner salt formation (oxonium), similar to that taking place with the amino acids.

curs. A study of the constants for the dibasic acids may therefore follow the lines laid down for the monobasic acids by considering the carboxyl group containing the un-ionized hydrogen as a negative substituent.

Malonic acid, from this point of view, is carboxyl acetic acid and should belong to the $\substack{\leftarrow \\ \rightarrow \\ \rightarrow}\mathrm{C{-}CO_2H}$ class. Its constant is found to be 0.164.[1] The following substituted malonic acids, with their ionization constants, have been measured: dimethylmalonic, 0.076; α,α-tetramethylenedicarboxylic, 0.080; isobutylmalonic, 0.090; octylmalonic, 0.095; heptylmalonic, 0.102; butylmalonic, 0.103; propylmalonic, 0.112; hexamethylene tetracarboxylic (1, 1, 3, 3), 0.12; isopropylmalonic, 0.127; ethylmalonic, 0.127; benzylmalonic, 0.151; allylmalonic, 0.154; ethylmethylmalonic, 0.164; β-benzoylisosuccinic, 0.250; methylbenzylmalonic, 0.266. These acids evidently all belong to the class $\substack{\leftarrow \\ \rightarrow \\ \rightarrow}\mathrm{C{-}CO_2H}$. Several acids, similarly constituted, have been found to give considerably greater dissociation constants. The value 0.74 was obtained for diethylmalonic and 1.46 for benzylethylmalonic. A comparison with the values obtained for ethylmethylmalonic (0.164) and for methylbenzylmalonic (0.266) indicates that the high values for the first two are due to some error as so large a difference is hardly to be expected for a change of CH_2 in these acids. On the other hand, the high values obtained for diallylmalonic acid (0.76) and dibenzylmalonic acid (4.1) may well be due to the constitutive effects of the substituting groups although measurements were not carried beyond a dilution of 256 liters.

Two substituted malonic acids have been measured which doubtless belong to the $\substack{\leftarrow \\ \leftarrow \\ \rightarrow}\mathrm{C{-}CO_2H}$ class: chloromalonic, 4, and α,α-trimethylenedicarboxylic, 2.1.

Succinic acid may be represented by the formula

$$(\alpha)\mathrm{HO_2C{-}CH_2} \rightarrow \mathrm{CH_2{-}CO\ H}(\beta).$$

If the α-hydrogen is ionized more easily than the β, succinic acid should belong to the $\substack{\leftarrow \\ \rightarrow \\ \rightarrow}\mathrm{C{-}CO_2H}$ class; if the the β more easily than the α, to the $\substack{\rightarrow \\ \rightarrow \\ \rightarrow}\mathrm{C{-}CO_2H}$ class. A study of the constants for succinic acid and the acids derived from it in which a hydrogen atom of one of the methylene groups is replaced by hydrocarbon radicals shows that the acids belong to the $\substack{\rightarrow \\ \rightarrow \\ \rightarrow}\mathrm{C{-}CO_2H}$ class (analogous to acetic acid), the negative carboxyl substituent in the β-position exerting a constitutive effect similar to that exerted by the halogens in the β-substituted propionic acids. The results for these acids are as follows: Succinic, 0.0068; isopropylsuccinic, 0.0075; asym. dimethylsuccinic, 0.0081; methylsuccinic, 0.0085; ethylsuccinic, 0.0086; isobutylsuccinic, 0.0088; propyl-

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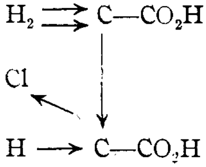
[1] Mean of the results given by Ostwald (0.158), Walden (0.163), and Bethmann (0.171). Berthelot found 0.165 at 17°.

succinic, 0.0089; benzylsuccinic, 0.0091; and allylsuccinic, 0.0109. The three acids, bromosuccinic 0.278, chlorosuccinic 0.284, and sym. bromomethylsuccinic 0.478, evidently belong to the $\begin{smallmatrix}\leftarrow\\ \rightarrow\\ \rightarrow\end{smallmatrix}$ C—CO_2 class analogous to chloroacetic acid and must be formluated (for the first named as example),



$$\begin{tikzcd}[row sep=small] & H_2 \rightrightarrows C\text{—}CO_2H \arrow[dd] \\ Cl & \\ & H \rightarrow C\text{—}CO_2H \arrow[ul] \end{tikzcd}$$

, in which each of the carbon atoms combined with a carboxyl has gained two and lost one corpuscle.

The symmetrical disubstituted succinic acids will not be taken up, as there are a number of isomers (stereochemical) known which are not sufficiently well characterized to make a discussion of them profitable. Furthermore, the fact that the three tartaric acids (*d*-, *l*-, and *i*-) have the same ionization constant (0.097) while mesotartaric acid has a different constant (0.060) shows that the presence of two asymmetric carbon atoms in an acid may result in differences in the values of the dissociation constants of acids which differ only in one being a racemic form (or mixture) and the other an internally compensated form, due doubtless to some effect at present entirely unknown. In the following tri- and tetra-substituted succinic acids, the presence of so many groups raises the constants to values greater than those found before for this class ($\begin{smallmatrix}\rightarrow\\ \rightarrow\\ \rightarrow\end{smallmatrix}$ C—CO_2H) but still considerably less than for the class $\begin{smallmatrix}\leftarrow\\ \rightarrow\\ \rightarrow\end{smallmatrix}$C—$CO_2H$: Trimethylsuccinic, 0.032; tetramethylsuccinic, 0.033; benzyldimethylsuccinic, 0.046; propyldimethylsuccinic, 0.055; ethyldimethylsuccinic, 0.056.

The higher homologs of the saturated dibasic acids may be considered as derived from the higher fatty acids containing a negative substituent which exerts only a minor influence upon the ionization constants as compared with the effect of the bonds. They should therefore belong to the $\begin{smallmatrix}\rightarrow\\ \rightarrow\\ \rightarrow\end{smallmatrix}$ C—CO_2H class, and, in fact, the constants for those measured are found to lie between 0.0022 and 0.0059. The following acids are included and are arranged in the order of increasing values for K: Camphoric, sebasic, azelaic, suberic, ω,ω′-dipropylpimelic, ω,ω′-diisopropylpimelic, *n*-pimelic, ω,ω′-dimethylpimelic, ω,ω′-diethylpimelic, adipic, glutaric, ω,ω′-dibenzylpimelic, α-methylglutaric, α,α′-diethylglutaric, β,β-dimethylglutaric, α,α′-dimethylglutaric, and β-methylglutaric.[1]

The effect of the hydroxyl group on the ionization constants of the dibasic acids is the same as for the monobasic acids, that is to say, the

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[1] α,α-Dimethyl-β-hydroxyglutaric, 0.0108, may also be placed in this class, the substituting groups exerting a greater effect on the constant.

negative character of the group raises the values, but for some constitutive or other effect the values are not less than where the negative substituent is a halogen atom or some other negative group. The constants for these hydroxy dibasic acids in which the second carboxyl group is not α to the first lie between those for the $\overset{\rightarrow}{\underset{\rightarrow}{\rightarrow}}\text{C—CO}_2\text{H}$ and the $\overset{\leftarrow}{\underset{\rightarrow}{\rightarrow}}\text{C—CO}_2\text{H}$ class, just as for the monobasic acids. This is illustrated by the acids: Malic, 0.039; mesotartaric, 0.060; and tartaric, 0.097. For those hydroxydibasic acids in which the two carboxyl groups are combined with the same carbon atom, the values of $K \times 10^5$ are found to correspond with those of the $\overset{\leftarrow}{\underset{\rightarrow}{\rightarrow}}\text{C—CO}_2\text{H}$ class; tartronic, 0.107, and benzyltartronic, 0.55, indicating that the effect of the hydroxyl group is not noticeable in the constants for these acids.

Some space may be devoted to the ester acids. With the higher homologs, the ethyl ester acids of sebasic 0.00143, suberic 0.00146, and adipic 0.0025, the constants show that they belong to the $\overset{\rightarrow}{\underset{\rightarrow}{\rightarrow}}\text{C—CO}_2\text{H}$ class, with the carboxyethyl group producing no appreciable effect. The ethyl ester acids of the malonic series, diethylmalonic 0.0231, dimethylmalonic 0.0304, methylmalonic 0.0387, ethylmalonic 0.0401, and malonic 0.0451, show that the action of the carboxyethyl group is similar to that of the hydroxyl (or ethoxyl, etc.) group in raising the constants above those for the $\overset{\rightarrow}{\underset{\rightarrow}{\rightarrow}}\text{C—CO}_2\text{H}$ class, but markedly below those for the $\overset{\leftarrow}{\underset{\rightarrow}{\rightarrow}}\text{C—CO}_2\text{H}$ class. If a specific constitutive reason is looked for, it may be due here, as indicated before, to the ether oxygen which is present in both groups.

The treatment of the succinic ester acids is complicated by the possibility of the existence of two isomeric ester acids in each case depending upon which of the two carboxyl group is esterified. The only substances of this series for which experimental values have been found are succinic ethyl ester acid 0.0030, and the methyl ester acids of succinic 0.0032, methylsuccinic 0.0039, *cis*-sym.-dimethylsuccinic 0.0046 (m. 38°), and *trans*-sym.-dimethylsuccinic 0.0061 (m. 49°). These results indicate that the ionization of these ester acids takes place from the group $\overset{\rightarrow}{\underset{\rightarrow}{\rightarrow}}\text{C—CO}_2\text{H}$, the carboxyethyl group in the β-position exerting only a small constitutive influence.

Few measurements are at hand for the polybasic saturated acids. Tricarballylic acid, 0.022, and $\omega,\alpha,\beta,\omega'$-butanetetracarboxylic acid, 0.040, indicate that in all probability the ionization takes place as in the simplest fatty acids from the group $\overset{\rightarrow}{\underset{\rightarrow}{\rightarrow}}\text{C—CO}_2\text{H}$ and that the presence of the carboxyl groups raises the constants above those obtained for the unsubstituted acids but that they are still below those for the $\leftrightarrows$ C—CO_2H class. No light is thrown on the question as to which of the carboxyl groups furnishes the hydrogen ion.

5. *Unsaturated Acids.*—The unsaturated acids will be taken up in the same way as the saturated, and the double bond will be assumed to have the same effect upon the dissociation constant as if it were made up of two single bonds. It will be seen that a perfectly rational classification follows from this method of treatment and that the acids containing a double bond between two carbon atoms fall into the same groups depending upon the direction of the valences and considering their influence as purely additive, as the saturated acids. Caution must be used, however, with regard to the data for some of the isomeric acids, as the methods of isolating the pure substances had not been worked out very satisfactorily when some of the measurements were made.

The following monobasic acids containing a double bond between the α- and β-carbon atoms in four cases and between the β- and γ- in one case may first be quoted: Methylethylacrylic, 0.0011; sorbic,[1] 0.0017; hydrosorbic, 0.0024; trimethylacrylic, 0.0039; and acrylic, 0.0056. These acids evidently may be considered as belonging to the $\rightrightarrows$ C—CO_2H class, whether the α-carbon atom is combined with the other atoms in the molecule by means of three single bonds or one double bond and one single bond.

Before going on to the isomeric unsaturated acids, a number of dibasic acids may be considered as being closely related to the unsaturated monobasic acids. Without going into the details of the structures of these acids, the following general remarks may suffice. The acids to be considered may be assigned to the $\rightrightarrows$ C—CO_2H class, the second carboxyl group acting merely as a negative constituent (not in the α-position). The double bond in the α,β-position exerts an influence on the β-carbon atom and therefore on the ionization constant similar to that exerted in β-bromopropionic acid, for example. The constitutive effects of the different groups may be considerable in special cases. Methylitaconic, 0.0095; itaconic, 0.012; tetraconic, 0.014; methylethylitaconic, 0.015; methylphenylitaconic, 0.024; Δ(β,γ)-hydromuconic, 0.010; dimethylglutaconic, 0.013; benzylglutaconic, 0.015; and glutaconic, 0.018. In these acids the factors mentioned above raise the ionization constants above the values found for the monobasic acids for the class indicated (just as in the saturated acids the same factors produce the same effect) but in no case is there a close approach to the constants for the class $\leftrightarrows$ C—CO_2H.

In the case of the isomeric unsaturated acids, a more detailed treatment is necessary. This can best be done with maleic and fumaric acids

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[1] Contains two double bonds, one α,β, the other γ,δ.

as here the substances were isolated in a state of purity early and therefore the measurements for finding the values of K may be considered to be accurate. Furthermore, the composition of the two acids is simple and it should be possible to draw perfectly definit conclusions. In the first paper[1] the conclusion was made very probable that fumaric acid should be assigned the structure $CO_2H.CH \rightleftarrows CH.CO_2H$ and maleic acid $CO_2H.CH \rightrightarrows CH.CO_2H$. Since the ionization constants refer only to one hydrogen ion and the carboxyl group may be treated as a negative substituent, fumaric acid should belong to the $\substack{\leftarrow\\ \rightarrow\\ \rightarrow}$ C—CO_2H class, and as a matter of fact, its constant was found to be 0.093.[2] Maleic acid may, however, ionize in one of two ways: either from the $\substack{\leftarrow\\ \leftarrow\\ \rightarrow}$ $C.CO_2H$ group or from the $\substack{\rightarrow\\ \rightarrow\\ \rightarrow}$ $C.CO_2H$ group. The ionization constants for the acids belonging to these classes differ widely, and the value found for maleic acid, 1.17,[3] shows that the ionization takes place in the first of the methods indicated and that maleic acid may be classed with di chloroacetic acid, and fumaric acid with monochloroacetic acid in considering the ionization of the first hydrogen.

The data for the other isomeric unsaturated acids are in less satisfactory shape. For crotonic and isocrotonic acids, the work on the latter was done with an impure acid, containing some of the former. The constant for crotonic acid was found to be 0.0020, showing its structure to be best represented by the formula $CH_3CH \rightrightarrows CH.CO_2H$. This is the more stable form of the two acids and the difference in structure as regards the double bond in comparison with the double bond in fumaric acid, the stable form of the isomeric dicarboxylic ethylenes, must be due to the difference in the groups attached to the carbons joined by the double bond in the former case, and their identity in the latter. The results obtained for the chlorocrotonic acids, assuming the constants to be correct, are difficult to interpret and it appears that in this case the constitutive effects predominate over the additive effects of the bonds, especially as the conditions for the stable form of the double bond are not well known and must be considered separately for every case in which the number and arrangement of the atoms in the two halves of the molecule separated by the double bond are not symmetrical.

Mesaconic acid (methylfumaric acid) has the constant 0.079, or one similar to that for fumaric acid. The constant for citraconic acid (methylmaleic acid) was found to be 0.34, larger than that for mesaconic acid, but apparently not enough larger to belong to the $\substack{\leftarrow\\ \leftarrow\\ \rightarrow}$ C—CO_2H class with certainty. The constant for ethylmaleic acid, 0.238, is of the same

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[1] *Loc. cit.*, p. 1643.

[2] By Ostwald; Berthelot found 0.100 at 22°.

[3] By Ostwald; Berthelot found 1.10 at 22°.

magnitude, and these two cases indicate that the substitution of an alkyl group for hydrogen in maleic acid decreases the constant considerably. The following results for substituted fumaric acids indicate clearly that these belong to the $\overset{\leftarrow}{\underset{\rightarrow}{\rightarrow}}$ C—CO_2H class: Ethylmesaconic, 0.093; isopropylmesaconic, 0.093; methylmesaconic, 0.094.

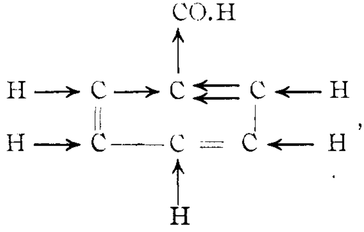
Benzalmalonic acid, 0.408, may be represented by the formula

$$C_6H_5CH \overset{\rightarrow}{\underset{\rightarrow}{\rightarrow}} C(CO_2H)\text{—}CO_2H.$$

The acids containing a triple bond can be disposed of briefly, as few have been measured. Tetrolic acid, 0.246, is to be best represented by the formula $CH_3.C \overset{\leftarrow}{\underset{\rightarrow}{\rightarrow}} C.CO_2H$, and phenylpropiolic acid, 0.59, by the similar formula $C_6H_5.C \overset{\leftarrow}{\underset{\rightarrow}{\rightarrow}} C.CO_2H$. The evidence obtained from the ionization constants leads to the same conclusion as to the usual structure of the triple bond, as did the study of the addition reactions with acetylenedicarboxylic acid considered in the first paper.[1]

6. *Aromatic Acids.*—The aromatic acids are taken to include those in which a carboxyl group from which the hydrogen is ionized is in direct combination with a carbon atom of the benzene nucleus. This carbon atom corresponds to the α-carbon atom in the saturated acids, and the bonds of this carbon atom are the ones which determin the ionization constant of the acid in question. It may be expected that a greater constitutive effect is exerted by the benzene ring on the constants. This is true to a certain extent as the general arrangement (or directions) of the valences and their influence upon each other between the carbon atoms in the ring are not known but the aromatic acids may be grouped in the same way as the aliphatic acids and the probable reciprocal influences of the bonds discussed without specifying the particular directions of all the valences. The benzene ring is assumed to contain alternate single and double bonds.

The ionization constant for benzoic acid was found to be 0.0067.[2] This indicates that benzoic acid belongs to the $\overset{\rightarrow}{\underset{\rightarrow}{\rightarrow}}$ C.CO_2H class, and that its graphic formula is



, the direction of the bonds indicated by dashes being unknown. Other aromatic acids in which the direction of the valences for carbon (1) is the same as for ben-

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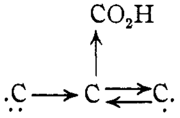
[1] *Loc. cit.*, p. 1644.

[2] By Euler, Ostwald found 0.0060.

zoic acid, but for which the arrangement of the other bonds is unknown except that no strong constitutive effect is manifested by the two carbon atoms in position (2) and that therefore the direction of the bonds in these is not such as would be expected if only negative groups were combined with them, are the following: *p*-Hydroxybenzoic, 0.0029; vanillic, 0.0030; isovânillic, 0.0032; anisic, 0.0032; veratric, 0.0036; mesitylenic, 0.0048; *m*-toluic, 0.0051; *p*-toluic, 0.0052; methylsalicylic, 0.0082; *m*-hydroxybenzoic, 0.0083; 1,3,5-dihydroxybenzoic, 0.0091; and *p*-chlorobenzoic, 0.0093.

The following acids may be assigned to the same class as benzoic acid: *m*-Fluorobenzoic, 0.0136; *m*-bromobenzoic, 0.0137; *m*-chlorobenzoic, 0.0155; *m*-iodobenzoic, 0.0163; *m*-cyanobenzoic, 0.0199; isophthalic, 0.0287; *m*-nitrobenzoic, 0.0345; *o*-toluic, 0.0120; *p*-nitrobenzoic, 0.0396; and 1,2,4-resorcylic, 0.0515. In the first seven of these acids, the negative substituent in position (3) (or corresponding to the γ-position in the aliphatic acids) apparently exerts a constitutive effect on the constant comparable with some of the effects exerted by negative constituents in the β-position of the aliphatic acids. This effect may be due to the influence of the negative constituents on the direction of the valences between the carbon atoms (2) and (3), causing the valences for (2) to assume directions, which, if present in aliphatic acids, would cause similar changes in the constants. Similar reasoning may be applied to the last three acids.

The following acids must be assigned to the $\overset{\longleftarrow}{\underset{\longrightarrow}{\longrightarrow}}$ C.CO$_2$H class, and the probable structure of part of the molecule may be formulated as



$$\underset{\cdot\cdot}{.\mathrm{C}} \longrightarrow \overset{\overset{\mathrm{CO_2H}}{\uparrow}}{\mathrm{C}} \rightleftarrows \underset{\cdot}{\mathrm{C}}.$$

: Salicylic, 0.102; 1,2,5-hydroxysalicylic, 0.108; 1,2,3-hydroxysalicylic, 0.114; *o*-phthalic, 0.121; *o*-chlorobenzoic, 0.132; *o*-bromobenzoic, 0.145; *m*,*m*-dinitrobenzoic, 0.162; and *o*-nitrobenzoic, 0.616.

The only acid which appears to belong to the $\overset{\longleftarrow}{\underset{\longrightarrow}{\longleftarrow}}$C.CO$_2$H class is 1,2,6-resorcylic, 5.0.

7. *Summary.*—Organic acids are divided into three classes in which the ionization constants ($K \times 10^5$) depend primarily upon the additive effects of the directive valences of the α-carbon atom: I. $\overset{\longrightarrow}{\underset{\longrightarrow}{\longrightarrow}}$ C.CO$_2$H, ionization constants less than 0.01; II. $\overset{\longleftarrow}{\underset{\longrightarrow}{\longrightarrow}}$ C.CO$_2$H, ionization constants 0.1–0.4; III. $\overset{\longleftarrow}{\underset{\longrightarrow}{\longleftarrow}}$ C.CO$_2$H, ionization constants greater than 2.

Substituents may exert constitutive effects resulting in constants for the acids between the values given for the classes, but a study of the composition should indicate in most cases the class to which the acid may be assigned.

The effects of double and triple bonds are assumed to be due to the additive actions of the valence directions making up these bonds. Fumaric acid is thus shown to be comparable in strength to an acid such as monochloroacetic and maleic acid to dichloroacetic.

BOSTON, April, 1911.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

POLARITY OF ELEMENTS AND RADICALS MEASURED IN TERMS OF A LOGARITHMIC FUNCTION OF THE IONIZATION CONSTANT.

BY C. G. DERICK.

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Introduction.

In recent years polarity of elements and radicals has been employed to explain many chemical behaviors. Since the overthrow of the dualistic theory, polarity has remained a rather indefinit term, one of "chemical instinct" rather than mathematical exactness. In 1901 W. A. Noyes and A. C. Lyon[1] made the following statement: "If we suppose, what seems not to be improbable, that all reactions involving the decomposition of molecules are preceded by an ionization of the parts of molecules, it would follow that elementary molecules as well may ionize into positive and negative parts." Ostwald[2] noted that certain groups and elements when substituted into acetic acid cause an increase or a decrease in its affinity constant. The former he called negative and the latter positive. Abegg,[3] in his article on "Valence and the Periodic System," stated that all elements are amphoteric, that is, exhibit positivity or negativity. He offers four criterions of polarity, ionization, hydrolysis, position in the periodic system, and finally the formula of the compound, in which case the maximum valence is the guide. This work supports the views of W. A. Noyes, referred to above. Finally, B. Flürscheim[4] has employed polarity in his studies of the distribution of affinity in the molecule of organic compounds. In a distinctly qualitative manner he has shown the value of the conception of polarity in interpreting certain properties of the organic molecule and it is in this branch of chemistry that polarity may be used most successfully in correlating chemical properties. In all these suggestions a more or less qualitative measure

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[1] THIS JOURNAL, 23, 460 (1901).

[2] *J. prakt. Chem.*, 31, 433 (1885); *Z. physik. Chem.*, 3, 170, 418 (1889). Also Nernst, "Theoretische Chemie," 6th Auflage, p. 510.

[3] *Z. anorg. Chem.*, **39**, 330 (1904).

[4] *J. Chem. Soc.*, **95**, 718 (1909); **97**, 84 (1910).