HOLLMAN

Correlation of Ionization and Structure

Chemistry

B. S.

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CORRELATION OF IONIZATION AND STRUCTURE

BY

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THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

EDWARD EMIL HOLLMAN

ENTITLED Correlation of Ionization and Structure.

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF BACHELOR OF SCIENCE

in chemistry

Clarence G. Derick
Instructor in Charge

APPROVED:

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HEAD OF DEPARTMENT OF

[Signature]
. CORRELATION OF CHEMICAL STRUCTURE WITH IONIZATION.

INTRODUCTION.

The means open to the chemist for solving the problem of chemical structure, so far at least as is known at the present day, fall directly into two classes,—chemical and physical. The chemical process consists in the preparation of a substance, or of a final substance whose structure is known, and in reasoning backward from this substance to the original, the act of reasoning being based, of course, on the authority of certain well-known, well-proven theories. This method, tho generally applicable, has its limitations. In some cases the preparation of a known derivative is a tedious process, requiring a relatively large amount of material, and destroying that material beyond recovery. In other cases the use of certain reagents is excluded, because of the possibility of their producing isomeric change either in the original compound or in the derivative. Sometimes the chemical process does not afford sufficient criterion for proof of structure. If this is the case physical means are resorted to. Among the physical means that can be applied to the problem are color, density, heat of combustion, solubility, melting point, optical properties, and finally electrical conductivity. Some of these devices, for instance color and density, can be used only to distinguish dynamic isomers, but electrical conductivity, with which this paper will deal exclusively, is generally applicable to all compounds which ionize even to the slightest extent.

Among the advantages of the electrical conductivity method
it might be noted that it rapid, and economical in that it does not destroy the substance under consideration and that only a small amount of the substance, less than a gram, is sufficient.

But this amount must be very pure if accurate results are to be hoped for; which, by the way, is not a disadvantage, but rather, in the end, a helpful necessity.

Electrical conductivity results directly from ionization, and it is the purpose of this investigation to show that a more intimate relation than has been discovered heretofore, exists between the ionization of a substance and its chemical structure, as has been pointed out by Derick(1). This paper deals in general with the straight-chain olefine acids, and in particular with allyl acetic acid, \( \text{CH}_3-\text{CH}-\text{CH}_2-\text{COOH} \), testing Derick's law of place influence by means of data obtained experimentally and bibliographically.

**HISTORICAL.**

Ostwald(2), in 1889, was the first to recognize the existence of a relation between the ionization of a substance and its chemical constitution, and attempted at that time to find a mathematical law, now known as Ostwald's factor law, which would define this relation in its lowest terms. The law is as follows:

\[
\frac{K\prime}{K_o} = \alpha
\]

where \( K_o \) is the ionization constant of the unsubstituted acid, and \( K\prime \) is that of the substituted acid with the substituent entering the \( \alpha \) position with respect to the carboxyl group. This method is continued for the \( \beta, \gamma \), and subsequent positions. Thus:

\[
\frac{K(\text{acetic})}{K(\text{propionic})} = \frac{K(\text{Cl propionic})}{K(\text{propionic})} = \frac{K(\text{Cl butyric})}{K(\text{butyric})} \quad \text{etc.}
\]

*accuracy in the absolute conductivity not in the place influence which does not require a high degree of accuracy.*
K. Drucker\(^{(2)}\) has tested out this law and finds that sometimes it holds and sometimes it does not. I, also, have found that Ostwald's factor law does not hold very rigidly among the straight-chain unsaturated acids, the greatest variation in the constant coming when the unsaturation is in the \(\alpha\)-position, as can be seen from column \(\%\) in Table I. It will further be seen that some of the constants relating to three different positions are very nearly the same, which fact alone would nullify the efficacy of this measure as a means of determining structure. I think that the reason that Ostwald's factor law does not, and cannot hold is because no attempt is made to isolate the influence of the entering molecule on the ionizing group.

To obtain the ionization constants used in making these calculations, \(K(\text{corr})\) in the table, corrections were made for the values of \(\lambda_{\alpha\text{H}}\) and \(\lambda_{\alpha\text{nH}}\), and for the value of the unit of resistance, (ohm = Siemens's unit \(\div 1.063\)), wherever necessary. The value of \(\lambda_{\alpha\text{H}}\) used was 350, and that of \(\lambda_{\alpha\text{nH}}\) was 51.2. The work was carried on at twenty-five degrees centigrade.

Derick(1) has shown that 'some function of the ionization constant may be taken as a relative measure of the combined direct and indirect influences of radicals on a given atom or molecule.' This function he finds to be \(\frac{\log K}{\log K} - 1\). Since this paper is dealing with unsaturated acids, the combined direct and indirect influence of unsaturation on a given radical may be found by varying the position of the double union and, at the same time, noting the effect on the ionization constant, because every atom in a compound affects this value additively. In this case we do not get the exact measure of the influence of the saturated radical on the ionizing group, but we get this value
<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>K (°C)</th>
<th>K (corr)</th>
<th>-log K</th>
<th>I (Influence)</th>
<th>Ostwald's Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Propionic</td>
<td>CH₃CH₂COOH</td>
<td>1.34×10⁻⁷</td>
<td>1.33×10⁻⁷</td>
<td>4.8661</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. Acrylic</td>
<td>CH₂=CHCOOH</td>
<td>5.60×10⁻⁹</td>
<td>5.40×10⁻⁹</td>
<td>4.2676</td>
<td>0.145 -- 0.142</td>
<td>4.1 -- 4.0</td>
</tr>
<tr>
<td>3. Butyric</td>
<td>CH₃CH₂CH₂COOH</td>
<td>1.48×10⁻⁹</td>
<td>1.47×10⁻⁹</td>
<td>4.6337</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4. Crotonic</td>
<td>CH₃CH=CHCOOH</td>
<td>2.04×10⁻⁷</td>
<td>1.85×10⁻⁷</td>
<td>4.7388</td>
<td>0.022 -- 0.021</td>
<td>1.3 -- 1.3 -- 1.3</td>
</tr>
<tr>
<td>5. Vinyl Acetic</td>
<td>CH₂=CHCH₂COOH</td>
<td>2.63×10⁻⁹</td>
<td>3.76×10⁻⁹</td>
<td>4.4246</td>
<td>0.063 -- 0.092</td>
<td>2.6 -- 2.6 -- 2.6</td>
</tr>
<tr>
<td>6. Valerianic</td>
<td>CH₃CH₂CH₂CH₂COOH</td>
<td>1.61×10⁻⁹</td>
<td>1.56×10⁻⁹</td>
<td>4.8069</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7. α-δ-Pentenic</td>
<td>CH₂=CH₂CH=CHCOOH</td>
<td>1.46×10⁻⁹</td>
<td>1.45×10⁻⁹</td>
<td>4.8386</td>
<td>0.0055 -- 0.0054</td>
<td>0.049 -- 0.040</td>
</tr>
<tr>
<td>8. β-γ-Pentenic</td>
<td>CH₂=CHCH₂CH₂COOH</td>
<td>3.36×10⁻¹⁰</td>
<td>3.30×10⁻¹⁰</td>
<td>4.8615</td>
<td>0.072 -- 0.074</td>
<td>2.1 -- 2.1</td>
</tr>
<tr>
<td>9. γ-δ-Pentenic</td>
<td>CH₃CH₂CH₂CH₂COOH</td>
<td>2.12×10⁻¹⁰</td>
<td>2.09×10⁻¹⁰</td>
<td>4.6794</td>
<td>0.027 -- 0.028</td>
<td>1.3 -- 1.3</td>
</tr>
<tr>
<td>10. Caproic</td>
<td>CH₃CH₂CH₂CH₂CH₂COOH</td>
<td>1.45×10⁻⁷</td>
<td>1.41×10⁻⁷</td>
<td>4.8508</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11. α-γ-Hexenic</td>
<td>CH₂=CH₂CH₂CH=CHCOOH</td>
<td>1.69×10⁻⁹</td>
<td>1.66×10⁻⁹</td>
<td>4.7307</td>
<td>0.025 -- 0.030</td>
<td>1.3 -- 1.4</td>
</tr>
<tr>
<td>12. β-γ-Hexenic</td>
<td>CH₂=CHCH₂CH₂CH₂COOH</td>
<td>2.41×10⁻⁹</td>
<td>2.32×10⁻⁹</td>
<td>4.6345</td>
<td>0.047 -- 0.051</td>
<td>1.6 -- 1.7</td>
</tr>
<tr>
<td>13. γ-δ-Hexenic</td>
<td>CH₂=CHCH₂CH₂CH₂COOH</td>
<td>2.64×10⁻⁹</td>
<td>2.61×10⁻⁹</td>
<td>4.5634</td>
<td>0.059 -- 0.063</td>
<td>1.9 -- 1.9</td>
</tr>
<tr>
<td>14. δ-ε-Hexenic</td>
<td>CH₂=CHCH₂CH₂CH₂COOH</td>
<td>1.74×10⁻⁹</td>
<td>1.70×10⁻⁹</td>
<td>4.7689</td>
<td>0.017 -- 0.022</td>
<td>1.2 -- 1.2</td>
</tr>
<tr>
<td>15. Sorbic</td>
<td>CH₂=CHCH=CHCH=CHCOOH</td>
<td>1.73×10⁻⁹</td>
<td>3.42×10⁻⁹</td>
<td>4.4660</td>
<td>0.094 -- 0.096</td>
<td>1.3 -- 1.3</td>
</tr>
<tr>
<td>16. Cinnamic</td>
<td>C₆H₅CH=CHCOOH</td>
<td>3.55×10⁻⁹</td>
<td>3.42×10⁻⁹</td>
<td>4.4660</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For the same acid, the different values in columns 6 and 7 are obtained by using different values of the unsubstituted acid.
minus the influence of two hydrogen atoms, but, since in the substituted acid, this is really the part present to affect the ionizing group, this only is the measure we wish to obtain.

Derick further develops a tentative law, which he calls the rule of thirds. The essence of the rule is this: the influence of the substituted atom in the \( \alpha, \beta, \gamma, \text{ etc.} \) positions on the ionizing group is as \( 1 : \frac{1}{3} : \frac{1}{3} \text{ etc.} \) respectively, the ratio being measured in terms of the place influence, \( I \). This rule will be treated later.

In the logarithmic function \( \frac{\log K}{\log K} = 1 \), Derick assumes that the total (direct and indirect) influence of each atom in the molecule on ionization is additive. If this is true, the ionization constant of any straight-chain acid can be calculated provided that the total, separate influences, of the various atoms of which the chain is composed, are known. The influence of the separate atoms is found by isolating that influence. For example, the ionization constant of the unsubstituted acid is measured, and then that of the substituted one. These values are then substituted in the following equations:-(taking \( \alpha \)-chloracetic and acetic acids as examples).

Where 'a' is a constant, \( I \) the influence, and \( K \) the ionization constant.

\[
I(\text{acetic acid}) = a \frac{1}{\log K(\text{acetic acid})}
\]

\[
I(\alpha\text{-Cl acetic}) = a \frac{1}{\log K(\alpha\text{-Cl acetic})}
\]

\[
I(\alpha\text{-Cl acetic}):I(\text{acetic}) = \frac{1}{\log K(\alpha\text{-Cl acetic})} : \frac{1}{\log K(\text{acetic})}
\]

\[
\frac{I(\alpha\text{-Cl acetic})}{I(\text{acetic})} = \frac{\log K(\text{acetic})}{\log K(\alpha\text{-Cl acetic})}
\]
Assuming the influence of all the atoms exclusive of the chlorine atom to be equal to one, the following equation is obtained:

\[ I(\neq Cl-LH) = \frac{\log K(acetic)}{\log K(\neq Cl acetic)} - 1. \]

which gives an isolated, and quantitative expression for the influence of the chlorine atom in the alpha position with respect to the carboxyl group (minus that of one hydrogen atom) on the ionization of straight-chain acids.

**EXPERIMENTAL.**

The Preparation of Allyl Acetic Acid and Its Sodium Salt.

The problem was to prepare as pure a product as possible, and to this extent the intermediate products formed were purified wherever it was deemed expedient.

I. Allyl Bromide:

PBr₃ was dropped into allyl alcohol. The action was vigorous but could be easily controlled. The whole was then refluxed for fifteen minutes to complete the reaction, and treated with Na₂CO₃ to destroy the HBr dissolved in the mixture. Yield: 73%. B.P. (allyl bromide): 76.3°C.

Malonic Acid Synthesis:

II. Allyl Malonic Ester:

The calculated amount of allyl bromide was added slowly thru a reflux condenser to a freshly prepared, alcoholic solution of sodium malonic ester. The action was very vigorous and a white precipitate of NaBr separated out. The whole was refluxed for one and one-half hours. The reformed alcohol was then distilled off, and the ester distilled over between 210-220°C.

III. Allyl Malonic Acid:

The allyl malonic ester obtained above was saponified with
twice the theoretical amount of KOH (1.25g KOH in 2g H₂O).
The saponification was complete after boiling for three hours as
was shown by a ether extraction. On evaporation of the ether
no residue oil was left. The yellow solution of the potassium
salt of allyl malonic acid was then carefully neutralized with
concentrated hydrochloric acid. A white precipitate formed
but this was found to be potassium chloride and was filtered off.
To the filtrate was then added a cold saturated solution of cal-
cium chloride until no more precipitate formed on heating a fil-
tered portion. This calcium salt was then filtered off and
pressed dry, moistened with a little water, and the free acid ob-
tained by adding concentrated hydrochloric acid until the whole
was in solution. The free acid was then extracted with ether.
On evaporation of the ether in a vacuum desiccator the allyl
malonic acid was obtained as a white, crystalline product. A
small amount of mother liquor was left; this was filtered off,
pressed into an unglazed clay plate, and the product recrystallized
twice from boiling C.P. benzene. Snow white crystals M.P. 103°C (corr)

IV. Allyl Acetic Acid:—

This allyl malonic acid was then placed in a 25cc. distilling
bulb with a long, upward-inclined condenser, immersed in a Wood's
metal bath, and maintained at 175-180°C. until no more carbon
dioxide was given off. The condenser was then inclined downwards
and the allyl acetic acid distilled off, and fractionated, most
coming over between 186-187°C.

V. The Preparation of the Sodium Salt of Allyl Acetic Acid.

The calculated amount of a freshly prepared solution of
sodium hydroxide in absolute alcohol of known strength was added
to allyl acetic acid, and the sodium salt crystallized out imme-
lately as a white solid. Then to destroy any free NaOH present a slight excess of the acid was added until blue litmus was turned slightly red. The sodium salt was then dried, and recrystallized twice from boiling absolute alcohol, and a snow white product was obtained which was dried in vacuum, powdered in an agate mortar, and kept in vacuum over calcium chloride to drive out all occluded vapors. This salt was then analysed and gave the following results:

<table>
<thead>
<tr>
<th>Wt. of Sample (grs.)</th>
<th>Wt. of Na₂SO₄ (grs.)</th>
<th>%Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3281</td>
<td>1.318</td>
<td>99.40</td>
</tr>
<tr>
<td>1.4234</td>
<td>1.2463</td>
<td>99.97</td>
</tr>
</tbody>
</table>

The conductivity of the acid and its sodium salt at different dilutions was then determined.

The Conductivity of Allyl Acetic Acid and its Sodium Salt.

All apparatus, with which the substances whose conductances were to be measured came into contact, was thoroughly steamed out and washed with conductivity water immediately before use. The sample of acid and salt, was weighed accurately on a calibrated, fine balance accurate to one tenth of a millegram, and the solutions on a large balance accurate to one hundredth of a gram. The conductivity water was prepared by redistilling pure water which had been heated to boiling with alkaline permanganate twenty-four hours before, and was collected at such a rate that half of it escaped as steam, the collection taking place only after about half of the total volume in the tank had distilled off. This last precaution removed all danger of contamination from ammonia in the water collected. The specific conductance, or $K$ of the water in no case exceeded $1.2 \times 10^{-6}$. All the measure-
ments of conductance were made on a calibrated, slidewire, Wheatstone bridge. The cell used for the salt and the acid was of the pipette form with platinum-black electrodes about two millimeters apart. The cell used for the water was of cylindrical form with removable, platinum electrodes. By means of this apparatus the resistance of the solution between the electrodes was obtained directly. The reciprocal of this value gave K, the conductivity; and K multiplied by the cell constant, \( \frac{1}{9} \), obtained from the conductivity of freshly crystallized, fused, powdered, and dried KCl, gave K, the specific conductance. Then, by means of the equation:

\[
\lambda = 1,000 K V,
\]

the value \( \lambda \) was obtained. From this value the ionization constant was calculated by using a somewhat modified form of Ostwald's dilution law: 

\[
K = \frac{\lambda^2}{V \lambda_{\alpha}(\lambda_{\omega-\lambda})}.
\]

Table II. shows the values obtained for both the acid and its sodium salt.

A rigorous test to apply to the results as shown in Table II., is to plot them. The general equation of a straight line passing thru two points is \( y = ax + b \). Ostwald's dilution law when reduced to this form becomes:

\[
\frac{1}{\lambda} = (C\lambda)^{n} + b.
\]

\( \frac{1}{\lambda} \) and \( (C\lambda)^{n} \) were then plotted against each other on a large scale in which the smallest square represented 0.1% of the smallest value of \( \frac{1}{\lambda} \). By this method two things are tested, the accuracy of the data, and the accuracy with which the mass law holds. For weak electrolytes such as allyl acetic acid, the value of \( n \) in the expression \( (C\lambda)^{n} \) is two, if the mass law holds. In the case of the sodium salt, however, which is a strong electrolyte, the value of \( n \) was taken as 1.45, the generally accepted value for salts of this type, and in all the plotted data on the sodium salt of allyl acetic acid this value gave the best straight line, tho all the values from 1.40 to 1.50 inclusive were tried.

According to Kohlrausch's law, at infinite dilution the fol-
### Table II.

Data for Allyl Acetic Acid \((25^\circ\text{C})\)

<table>
<thead>
<tr>
<th>R.</th>
<th>K.</th>
<th>(K_0)</th>
<th>(\lambda)</th>
<th>(\frac{1}{K})</th>
<th>((\text{ioniz. const.)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>.02 Normal</td>
<td>356.3</td>
<td>12.02</td>
<td>.083200</td>
<td>.2404</td>
<td>2.06(\times)10(^{-5})</td>
</tr>
<tr>
<td>1) 356.3</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>2) 356.5</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>.01 Normal</td>
<td>362.2</td>
<td>16.96</td>
<td>.05884</td>
<td>.1700</td>
<td>2.09(\times)10(^{-5})</td>
</tr>
<tr>
<td>1) 362.2</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>2) 362.0</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>.005 Normal</td>
<td>516.5</td>
<td>23.76</td>
<td>.04210</td>
<td>1.188</td>
<td>2.08(\times)10(^{-5})</td>
</tr>
<tr>
<td>1) 516.5</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>2) 516.5</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>.0025 Normal</td>
<td>739.2</td>
<td>33.06</td>
<td>.03697</td>
<td>.08265</td>
<td>2.07(\times)10(^{-5})</td>
</tr>
<tr>
<td>1) 739.2</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>2) 746.0</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>.001 Normal</td>
<td>1212</td>
<td>43.92</td>
<td>.03004</td>
<td>.04992</td>
<td>1.98(\times)10(^{-5})</td>
</tr>
<tr>
<td>1) 1212</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>2) 1212</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>.0005 Normal</td>
<td>1782</td>
<td>67.2</td>
<td>.01428</td>
<td>.0336</td>
<td>1.90(\times)10(^{-5})</td>
</tr>
<tr>
<td>1) 1782</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>2) 1782</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

\(K\text{(ave.)}= 2.03\times10^{-5}\)

Data for Sodium Salt

| .02 Normal  | 42.30 | .02364 | .0014977 | .74.88 | .013353 | 1.1928 |
| 42.30 | .02364 | .0014977 | .74.88 | .013353 | 1.1928 |
| .01 Normal  | 81.75 | .01824 | .0007533 | .75.33 | .013274 | .86032 |
| 81.75 | .01824 | .0007533 | .75.33 | .013274 | .86032 |
| .0075 Normal | 107.6 | .03293 | .9055747 | .76.63 | .01305 | .77936 |
| 107.6 | .03293 | .9055747 | .76.63 | .01305 | .77936 |
| .005 Normal  | 152.05 | .008387 | .0003884 | .77.38 | .012872 | .65341 |
| 152.05 | .008387 | .0003884 | .77.38 | .012872 | .65341 |
| .0025 Normal | 311.0 | .03215 | .001981 | .79.34 | .01262 | .46361 |
| 311.0 | .03215 | .001981 | .79.34 | .01262 | .46361 |
| .001 Normal  | 761.5 | .01313 | .000802 | .80.24 | .012462 | .32135 |
| 761.5 | .01313 | .000802 | .80.24 | .012462 | .32135 |
| .0005 Normal | 1494 | .00689 | .000403 | .80.68 | .012395 | .23582 |
| 1494 | .00689 | .000403 | .80.68 | .012395 | .23582 |
lowing equations hold.
\[
\lambda_\omega(\text{RCOONa}) = \lambda_\omega(\text{RCOO}) + \lambda_\omega(\text{Na}^+) \\
\lambda_\omega(\text{RCOOH}) = \lambda_\omega(\text{RCOO}^-) + \lambda_\omega(\text{H}^+) \\
\therefore \lambda_\omega(\text{RCOOH}) = \lambda_\omega(\text{RCOONa}) - \lambda_\omega(\text{Na}^+) + \lambda_\omega(\text{H}^+). 
\]
Since \( \lambda_\omega(\text{RCOONa}) \) can be determined accurately experimentally, it is a simple matter to obtain \( \lambda_\omega(\text{RCOOH}) \). From this value the ionization constant is determined as shown above.

To obtain \( \lambda_\omega(\text{RCOONa}) \) the best straight line thru the last three points on the curve, (that is: \(-C=0.0025, 0.001, \text{and} 0.0005\) ), was extrapolated to \( C=0 \). With my own experimental data the best straight line taken in almost any way gave a \( \lambda_\omega(\text{RCOONa}) \) which differed from all others by less than the experimental error, the difference in \( \lambda_\omega(\text{RCOONa}) \), taking extreme values, being \( 0.4\% \). By this means we obtained the values \( \lambda_\omega = 0.01220 \), and \( \lambda_\omega(\text{RCOONa}) = 82.0 \), and therefore \( \lambda_\omega(\text{RCOOH}) = 381 \).

CONCLUSION.

1. By glancing at column six in Table I., it will be seen that the double bond exerts the maximum influence when in the \( \beta-\gamma \) position with respect to the carboxyl group. Fichter and Pfister (4) were the first to call attention to this fact, and although all the data they used were corrected, this fact still remains the same.

2. It will further be seen that only in one case does the rule of thirds hold, and that is in going from the \( \beta-\gamma \), to the \( \gamma-\delta \) position, provided the data are accurate. Below are the two values of \( K \) calculated by this rule.

\[
K(\gamma-\delta \text{ Pentenic acid}) \text{ from } I(\beta-\gamma(\omega)) \text{ Pentenic acid: -} \\
I(\gamma-\delta) = 0.072, \frac{0.072}{3} = 0.024 \\
-4.8069 = -4.6034 = 5.3057 - 10 \cdot K = 2.02 \times 10^{-5} \\
K(\text{exp}) = 2.09 \times 10^{-6} 
\]
K(y-δ Hexonic acid) from I(α-γ(w)) Hexonic acid:

\[ I(\alpha-\gamma(w)) = 0.058, \frac{0.058}{3} = 0.0196 \]
\[ \frac{-4.8506}{1.0196} = -4.7575 = 5.2525 \times 10^{-9} \]
\[ K = 1.79 \times 10^{-5} \]

\[ K(exp) = 1.70 \times 10^{-5} \]

3. It will also be noticed that the maximum of influence is highest in the shortest chain, and decreases as the length of the chain increases. This is best seen in the following arrangement:

\[ CH_2CHCH_2COOH \quad \text{-----} \quad 0.093 \]
\[ CH_2CH=CHCH_2COOH \quad \text{-----} \quad 0.073 \]
\[ CH_3CH_2CH=CHCH_2COOH \quad \text{-----} \quad 0.059 \]

Hence the influence (I), for the (β-γ(α)) is not independent of the pair of acids from which it is calculated as Derick found for Cl,Br,(OH), (=NOH).

4. Additive relation: - That the influence which the double union exerts on the ionization of a substance is additive, that is, that it can be added to the sum of the influences which all the other molecules exert in the same direction, has not been found to be the case, at least with the data obtainable. The additive relation was tested by comparing the calculated with the measured ionization constants of sorbic acid, and of cinnamic acid. The influence of an α-β double union, as can be seen from Table I, is .025 (or .030) in a chain of six carbon atoms, and that of a γ-δ double union is .017 (or .022). The sum of these gives .042 (or .052). The measured value (2) is .016. In the case of cinnamic acid a similar proportional difference will be noticed. The influence of the β phenyl group (1) is .043, and that of an α-β double union from Table I, in a chain of three carbon atoms is .145. The sum of these gives .188, while the measured value is .094 (2). The following table shows these
results more clearly.

<table>
<thead>
<tr>
<th>Name</th>
<th>$K$</th>
<th>$-\log K$</th>
<th>$I$</th>
<th>$K_{\text{calculated}}$ from $0.042$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-Hexenic</td>
<td>$1.86 \times 10^5$</td>
<td>$-4.7307$</td>
<td>$0.035 (\text{or} 0.030)$</td>
<td></td>
</tr>
<tr>
<td>$\gamma$-Hexenic</td>
<td>$1.70 \times 10^5$</td>
<td>$-4.7689$</td>
<td>$0.017 (\text{or} 0.022)$</td>
<td></td>
</tr>
<tr>
<td>Sorbic</td>
<td>$1.73 \times 10^5$</td>
<td>$-4.7620$</td>
<td>$0.042 (\text{or} 0.052)$</td>
<td>$2.21 \times 10^{-5}$</td>
</tr>
<tr>
<td>$\alpha$-Phenyl propionic</td>
<td>$2.3 \times 10^{-5}$</td>
<td>$-4.637$</td>
<td>$0.043$</td>
<td></td>
</tr>
<tr>
<td>Acrylic</td>
<td>$5.40 \times 10^{-6}$</td>
<td>$-4.2676$</td>
<td>$0.145$</td>
<td>$0.038$</td>
</tr>
<tr>
<td>Cinnamic</td>
<td>$3.42 \times 10^{-5}$</td>
<td>$-4.4660$</td>
<td>$0.034$</td>
<td>$7.71 \times 10^{-8}$</td>
</tr>
</tbody>
</table>

Altho the above results seem to disprove the additive relation when applied to the double union, conclusions can hardly be drawn, because of the fact that so little work has been done on these acids, and until the data on these acids is checked up by several more investigators, it will not be safe to do so.
BIBLIOGRAPHY.


