potassium or lithium ethylate; namely, $K_i = 0.501$, $K_i = 0.501$ and $K_i = 0.496$, respectively.

(4) The constants, K_m, expressing the activity of the nonionized molecule of the metallic ethylate, have been found to be very close for sodium and potassium ethylates, namely, $K_m = 0.693$ and $K_m = 0.701$, respectively, but somewhat lower for lithium ethylate, $K_m = 0.478$, which is practically the same as that found for the ethylate ion, $K_i = 0.496$ in the case of lithium ethylate.

(5) Making use of the above considerations, satisfactory explanations have been offered for the approximate equality of the velocity constants, K_N, found for sodium and potassium ethylates, as well as for the deviation of the lithium ethylate constant from this value; for the fact that the molar constants, K_N, for lithium ethylate remain unchanged with dilution, while the same values for potassium ethylate and sodium ethylate drop considerably as the concentration decreases; and for the nearly identical value assumed by the velocity constants for all three ethylates in very dilute solutions.

(6) The averaged values of the constants for the ionic and molecular activities have been substituted in the equation $K_N = K_i\alpha + K_m(1 - \alpha)$ and these calculated values of K_N have been compared with those found experimentally. The average deviation is about 1.5 per cent.

Strong support of the theory here presented is found in unpublished work by Dr. C. N. Myers, on the formation of imido-esters from nitriles, catalysed by metallic ethylates; particularly important is the fact that the data obtained in very dilute solutions harmonized perfectly with the theory. Dr. Myers' work will be published in the near future.

MADISON, WIS.

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY, UNIVERSITY OF ILLINOIS.]

THE CORRELATION OF IONIZATION AND STRUCTURE IN UNSATURATED ACIDS.

BY C. G. DERICK AND OLIVER KAMM.[1]

Received December 23, 1916.

This research is a part of the general investigation of the correlation of ionization and atomic linking structure which has been in progress in this laboratory during the past five years. The laboratory investigation of this general problem has been concerned chiefly with the study of the effect, from the standpoint of ionization constants, of the substitution of a given atom or group of atoms into the paraffin monocarboxylic acids. In this field the probability of a correlation between the position

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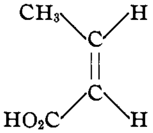
[1] A chapter from a thesis presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Illinois (Kamm, 1915). See also THIS JOURNAL, **38**, 400 (1916).

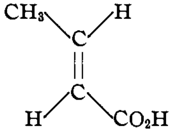
of the substituent and the ionization constant of the acid has been clearly demonstrated[1] from the existing data. No such correlation, however, was found to exist in the case of the unsaturated acids, for this class of compounds furnished the exceptions to the general rules. So striking are these contradictions that special theories, like those of Flürscheim,[2] have been advanced to explain them.

Historical Part.

Soon after Wislicenus[3] had expanded and applied the hypothesis of van't Hoff and Le Bel concerning the space arrangements of the four valences of the carbon atom, Ostwald[4] began the investigation of the compounds studied by Wislicenus from the standpoint of ionization, in order to assign the proper structures to individual isomers by means of the application of conductivity measurements. Adopting the formulas assigned by Wislicenus to crotonic and isocrotonic acids, Ostwald assigned analogous structures to other unsaturated acids.

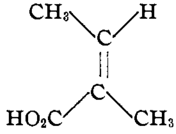


Crotonic acid, $K_a^{25^\circ} = 2.04 \times 10^{-5}$.

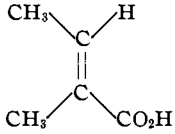


Isocrotonic acid, $K_a^{25^\circ} = 3.6 \times 10^{-5}$.

One of the isomeric methyl crotonic acids (angelic acid) has an ionization constant of $K_a^{25^\circ} = 5.0 \times 10^{-5}$ and the other (tiglic acid) of $K_a^{25^\circ} = 9.6 \times 10^{-6}$. On the basis that the stronger acid is the one having a hydrogen in close proximity to the carboxyl group, Ostwald assigned the following formulas to the two isomers:



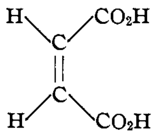
Tiglic acid.



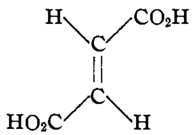
Angelic acid.

Similarly, other unsaturated acids were considered.

In the case of maleic and fumaric acids,[5]



Maleic acid, $K_a^{25^\circ} = 1.17 \times 10^{-2}$.



Fumaric acid, $K_a^{25^\circ} = 9.3 \times 10^{-4}$.

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[1] THIS JOURNAL, **33**, 1167, 1181 (1911).

[2] *J. Chem. Soc.*, **95**, 718 (1909).

[3] *Kgl. Sächs. Ges. d. Wiss.*, **24**, 1 (1887); *Z. physik. Chem.*, **3**, 241 (1889).

[4] *Z. physik. Chem.*, **3**, 241 (1889).

[5] *Ibid.*, pp. 380–381.

the one having the two carboxyl groups on the same side of the plane of the double union was found to be the stronger acid, and this fact was, therefore, used to distinguish between analogous isomers. It is thus apparent that the ionization constant measures the indirect (space) influence as well as the direct (chain) influence of a given constituent.

With the work of Fichter and Pfister,[1] a distinct advance is made in this field and the generalization is made that β,γ unsaturated acids possess larger ionization constants than the α,β-isomers. Fichter and Pfister have also suggested that the double union does not behave like a negative substituent, for in the latter case there is an uninterrupted decrease in ionization constant as the negative substituent is removed farther from the carboxyl group. Fichter and Pfister have demonstrated that this behavior is a general one which holds for chain acids as well as for cyclic acids. The effect of geometrical isomerism due to the double union was not considered. Recent treatments of this part of the subject, however, have been given by Roth and Stoermer[2] and also by Szyszkowski.[3]

The explanation offered by Fichter and Pfister for the low ionization constants of α,β unsaturated acids is based upon the Thiele Partial Valence Theory.[4] This view is also expressed by the writers on the basis of their conductivity measurements. According to Thiele, α,β unsaturated acids contain a conjugated system of double unions. Thus we are here dealing with more saturated and more stable compounds than in the case of the β,γ unsaturated acids and we should expect the better neutralized compounds to be also more stable toward ionization. The Thiele theory, therefore, may predict irregularities of this nature.

An altogether different explanation of the phenomenon discussed above has been offered by Michael,[5] who believes that the double union does behave like a negative substituent. According to him, the apparent contradictions are due to the fact that other investigators have used the wrong scale of influence.

Theoretical Part.

A preliminary study of the ionization constants of unsaturated acids reveals the fact that no general quantitative correlation sufficiently accurate to be of value for the prediction of the structures of unknown compounds appears to exist between the ionization constants and the atomic linking structures of these acids. The reason for this may be found partly in the fact that the experimental data may be somewhat inaccurate but more probably is to be sought in the fact that we have neglected the possibility of *cis-trans* isomerism. In some cases, we may be

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[1] *Ann.*, 334, 201 (1904); 348, 257 (1906).

[2] *Ber.*, 46, 260 (1913).

[3] *Z. physik. Chem.* 22, 180 (1897).

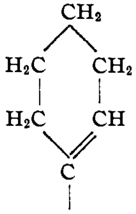
[4] *Ann.*, 306, 87 (1899).

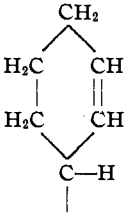
[5] THIS JOURNAL, 34, 849 (1912).

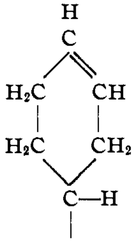
comparing the ionization constant of a *cis*-acid with that of an acid which is really a *trans*-isomer; in many cases, especially when the unsaturation is farther removed than the α,β position, we may be dealing with a mixture of geometrical isomers; and finally, we are not justified in comparing the unsaturated with the corresponding saturated acids, since, in the former, the positions of certain groups in space are fixed, whereas in the saturated acid, free rotation between the carbon atoms is possible, and this relation would vary for each pair of acids measured.

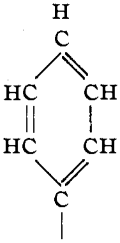
Because of these complicating influences, the present investigation deals with acids in which *cis-trans* isomerism due to the double union will not interfere. To make this possible, acids having the unsaturation in a ring of carbon atoms have been chosen. In determining the effect of a given double union, the ionization constant may, therefore, be referred to the hydrogenated acid which has its atoms in approximately the same space arrangement. The present work has been in the naphthalene series partly for this reason, and partly because of the fact that in this series the speed of reaction is slow and consequently the acids may be prepared in a pure condition; that is, rearrangements and oxidations are less liable to take place.

The possibilities of ionization data for the prediction of structure may be illustrated by the following example: If we determine quantitatively the separate effects of the double unions in the three tetrahydrobenzoic acids[1] (I, II and III), we might be able to determine whether benzoic acid has the Kekulé stucture (IV) since the latter formula contains the three double unions (Δ^1, Δ^2, and Δ^3) represented in the tetrahydrobenzoic acids above. Before it is possible to prove such a case, it would, however, first be necessary to determine whether the influences of the double unions are really additive. This information could be gained from the ionization constants of the various dihydrobenzoic acids.


(I).


(II).


(III).


(IV).

The present investigation has not gone as far as this; but it may throw some light upon the question of whether the above method of attack is

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[1] The ionization constants of two of these acids have been measured, *Ann.*, 271, 231-84 (1893).

feasible. It has attempted to determine whether the place influence of a double union in a given position in a carbon ring is constant.

Experimental Part.

Preparation and Purification of the Acids Measured.—The methods used for the preparation and purification as well as for the proof of structure of the acids studied in this work have already been described in detail.[1] Final purification always took place in well-steamed flasks of Jena glass. Usually the centrifuge was used in preference to the suction pump for the separation of the mother liquor from the crystals. The alcohol and acetone solutions used for the final purifications were of such purity that, when added to conductivity water, they did not appreciably change its conductance. In general, two samples of each acid were used in the measurements, one of which had received its final crystallization from aqueous solvents and the other from organic solvents. For this purpose, low-boiling ligroin was used in most cases, the latter having been redistilled and its purity tested by shaking it with conductivity water of known purity and then again measuring the conductivity.

The Conductivity Water.—Ordinary distilled water was redistilled from an alkaline permanganate solution, the first portions containing ammonia being discarded. It was collected hot in four-liter resistance-glass flasks which had been used for this purpose during a number of years. The still used was that in the Physical Division of this laboratory,[2] and with its use it was easily possible to obtain water having a specific conductance of 0.5 to 0.8×10^{-6} reciprocal ohms.

Apparatus.—The thermostat used consisted of a four-liter Dewar bulb fitted with a stirrer, cooling coil, and electrical heating coil. With this arrangement, it was easily possible to maintain the temperature of the bath within 0.01° of the desired temperature. The Kohlrausch method[3] was used for the measurement of conductivity. Both the bridge, which was of the drum type manufactured by Leeds and Northrup Co., as well as the Decade resistance boxes, were calibrated. A distinct improvement consisted in the use of the Paul telephone, manufactured by Robert W. Paul, of New Southgate, London, tuned to 1000 cycles, and possessing a resistance of 150 ohms. With the use of this instrument, extremely satisfactory end points could be obtained, falling well within the desired precision of 0.1%.

The Conductivity Cells.—These were of the pipet type. The usual salt-acid cell with platinized electrodes was not used since it was found possible to obtain equally accurate and often better end points by using cells with unplatinized electrodes, provided several cells with

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[1] This Journal, 38, 400, 419 (1916).

[2] *Ibid.*, 33, 1688 (1911); 35, 751 (1913).

[3] Kohlrausch and Holborn, "Leitvermögen der Elektrolyte," Leipzig, 1898.

varying capacities were used during the course of the dilutions. For concentrations above 0.0005 N a cell with a constant of 0.1031 was used, while through concentrations of 0.0005 N to 0.0001 N a cell with a constant of 0.01950 was used. By using unplatinized electrodes, the catalytic oxidation of the unsaturated acids was prevented. The cell constants were determined by several comparisons with the salt-acid cell, the constant of the latter having been obtained with standard potassium chloride solutions.

Preparation of Solutions.—The usual volumetric method for the determination of the normality of the solutions was not followed because of the very slight solubility of most of the acids measured, the solutions titrated being too dilute to give satisfactory end points. Instead, the sample of acid was weighed and water added to bring the solution up to the desired standard weight. The original solution as well as the dilutions were made up by weight, and for this reason a table of specific gravities is given in case it is thought desirable to change the concentrations into terms of volume normal. In each case the first solution was made up in a flask in which conductivity water was collected initially, thus rendering a transfer of the water for the first concentration unnecessary.

In order to weigh the sample with sufficient accuracy, at least 0.1000 g. of material and preferably a larger weight was used. For this reason it was often desirable to prepare as much as two liters of the first solution in the case of the less soluble acids.

Because of the difficulty of dissolving the acids, it was often found necessary to warm the solutions slightly on an electrical hot plate. In some cases, the weighed sample was added directly to the conductivity water before the latter had cooled to room temperature, first, however, withdrawing a sample for measurement.

An attempt was initially made to weigh out the material into a steamed flask, and to dissolve it by the addition of 1 cc. of pure ethyl alcohol or acetone, quickly reprecipitating it in a finely divided form, in which case it will dissolve readily, by the addition of the conductivity water. It was found, however, that a concentration of 0.1% of alcohol changed the conductivity of the solution by about 0.4% and hence this method could not be used. This result is in agreement with the observations of others.[1]

All the conductivity measurements have been made at a temperature of 25° ± 0.01°.

Specific Gravities of the Solutions.—If it is desired to change the concentrations given in the following tables into terms of volume normal instead of weight normal, the following specific gravities may be used:

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[1] THIS JOURNAL, 36, 2243 (1914).

TABLE I.

Concentration.	Sp. gr. $d_{25°}^{25°}$.	Concentration.	Sp. gr. $d_{25°}^{25°}$.
0.004 *N*	1.00014	0.0005 *N*	1.00002
0.002 *N*	1.00008	0.00025 *N*	1.00000
0.001 *N*	1.00004	0.000125 *N*	1.00000

The acid used for the above determinations was Δ^2-dihydronaphthoic acid-1. The results will serve for the densities of corresponding solutions of the other naphthoic acids, as was found by actual measurement in several cases.

Ionization Constants of β-Naphthoic Acid and of the Reduced α- and β-Naphthoic Acids.

In the calculation of the ionization constants as given in the following tables, the values for the conductivity at infinite dilution (λ_o) was calculated from the Ostwald rule.[1] The values used are: 377 for β-naphthoic acid, 376 for the dihydronaphthoic acids, and 375 for the tetrahydro acids. In the tables given below,

C = concentration of the acid.

λ = equivalent conductance at 25° at the concentration C uncorrected for the conductivity of the water used.

K = ionization constant calculated according to the equation

$$K = \frac{C\lambda^2}{\lambda_o\ (\lambda_o - \lambda)}.$$

β-Naphthoic Acid.—This acid has been measured by both Bader[2] and by Bethmann.[3] The values for $K_a^{25°}$ found are as follows:

$K_a^{25°} = 5.23 \times 10^{-5}$ (Bader).

$K_a^{25°} = 6.78 \times 10^{-5}$ (Bethmann).

Each one of the above values is, however, based upon measurements at only one dilution. The reason for this is the extremely slight solubility of the acid (less than one part in 30,000 parts water).

Because of the disagreement in the values given above, the measurements on this acid have been repeated and an attempt has been made to measure it at varying cncentrations.

TABLE II.

β-Naphthoic Acid. M. p. 185.5°.

Water used = 0.7×10^{-6}.

C.	λ.	$K_a^{25°}$.
0.0003 *N*	142.7	6.92×10^{-5}
0.0002 *N*	165.3	6.85×10^{-5}
0.0001 *N*	206.8	6.67×10^{-5}

TABLE III.

Δ'-Dihydronaphthoic Acid-2. M. p. 118.5°.

Water used = 0.7×10^{-6}.

C.	λ.	$K_a^{25°}$.
0.0005 *N*	80.57	2.92×10^{-5}
0.00025 *N*	108.3	2.91×10^{-5}
0.000125 *N*	142.56	2.90×10^{-5}

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[1] See Lundén's "Affinitätsmessungen an Schwachen Säuren und Basen," *Sammlung Chemischer und Chem. tech. Vorträge,* 14, 9 (1909).

[2] *Z. physik. Chem.*, 6, 311 (1890).

[3] *Ibid.*, 5, 399 (1890).

Dihydro- and Tetrahydronaphthoic Acids.—The ionization constants of five dihydro and of the two *ac*-tetrahydronaphthoic acids were determined. Most of these acids have been measured before[1] but it was considered advisable to redetermine their constants before drawing conclusions in regard to the correlation of ionization and structure.

The ionization constant of the new isomeric dihydro acid thus differs only slightly from the value (uncorr.) given by Bader, for the other isomer which has a double union in the Δ^1-position with respect to the carboxyl group, *i. e.*, the so-called Δ^2-dihydronaphthoic acid-2. A redetermination of the constant of the latter has given results somewhat lower than expected from the ionization constant of the tetrahydro acid and for this reason it is hoped to repeat the measurements.

TABLE IV.

Δ^2-Dihydronaphthoic Acid-2.

M. p. 161°.

Water used = 0.65×10^{-6}.

C.	λ.	$K_a^{25°}$.
0.0005 *N*	76.4	2.59×10^{-5}
0.00025 *N*	102.3	2.54×10^{-5}
0.000125 *N*	134.4	2.49×10^{-5}

TABLE V.

Δ^3-Dihydronaphthoic Acid-2.

M. p. 101.2°.

Water used = 0.55×10^{-6}.

C.	λ.	$K_a^{25°}$.
0.002 *N*	58.86	5.81×10^{-5}
0.001 *N*	80.19	5.78×10^{-5}
0.0005 *N*	107.43	5.72×10^{-5}
0.00025 *N*	141.2	5.65×10^{-5}
0.000125 *N*	180.7	5.56×10^{-5}

TABLE VI.

ac-Tetrahydronaphthoic Acid-2.

M. p. 96°.

Water used = 0.6×10^{-6}.

C.	λ.	$K_a^{25°}$.
0.003 *N*	32.60	2.48×10^{-5}
0.002 *N*	39.66	2.49×10^{-5}
0.001 *N*	54.21	2.44×10^{-5}
0.0005 *N*	73.94	2.41×10^{-5}

TABLE VII.

Δ^1-Dihydronaphthoic Acid-1.

M. p. 121.5°.

Water used = 0.65×10^{-6}.

C.	λ.	$K_a^{25°}$.
0.001 *N*	92.19	7.96×10^{-5}
0.0005 *N*	122.66	7.90×10^{-5}
0.00025 *N*	159.47	7.81×10^{-5}
0.000125 *N*	200.5	7.62×10^{-5}

TABLE VIII.

Δ^2-Dihydronaphthoic Acid-1.

M. p. 86°.

Water used = 0.84×10^{-6}.

C.	λ.	$K_a^{25°}$.
0.004 *N*	59.02	11.69×10^{-5}
0.002 *N*	80.3	11.60×10^{-5}
0.001 *N*	107.8	11.52×10^{-5}
0.0005 *N*	141.85	11.43×10^{-5}
0.00025 *N*	181.66	11.3×10^{-5}
0.000125 *N*	224.62	11.1×10^{-5}

TABLE IX.

ac-Tetrahydronaphthoic Acid-1.

M. p. 85°.

Water used = 0.8×10^{-6}.

C.	λ.	$K_a^{25°}$.
0.002 *N*	52.3	4.49×10^{-5}
0.001 *N*	71.4	4.45×10^{-5}
0.0005 *N*	96.06	4.39×10^{-5}
0.00025 *N*	127.7	4.37×10^{-5}
0.000125 *N*	165.3	4.31×10^{-5}

Δ^2-Dihydronaphthoic acid-1 is rapidly decomposed if its solution is measured with platinized electrodes. The decomposition is probably an oxidation, which is followed by the loss of carbon dioxide and the forma-

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[1] Bethmann and Bader, *Loc. cit.*

tion of naphthalene. The above values were, of course, obtained with the unplatinized electrodes. A similar difficulty is reported by Ostwald[1] in the measurement of formic acid.

Discussion of Results.

The following ratios show that the value for a Δ^2-double bond in the cyclic acids is fairly constant whereas in the unsaturated aliphatic acids no such regularity is found:

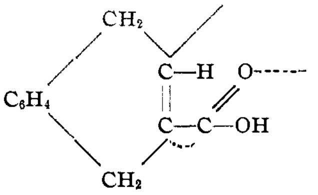
$$\frac{\text{K for } \Delta^3\text{ *-dihydronaphthoic acid-2}}{\text{K for } ac\text{-tetrahydronaphthoic acid-2}} = \frac{5.74}{2.47} = 2.33$$

$$\frac{\text{K for } \Delta^2\text{-dihydronaphthoic acid-1}}{\text{K for } ac\text{-tetrahydronaphthoic acid-1}} = \frac{11.6}{4.43} = 2.61$$

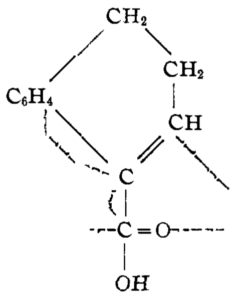
$$\frac{\text{K for } \Delta^2\text{-tetrahydrobenzoic acid}}{\text{K for hexahydrobenzoic acid}} = \frac{3.05}{1.28} = 2.38$$

This regularity is not found in the case of the Δ^1 double unions, and the explanation for the deviation is sought in the fact that in the latter case we are dealing with acids in which the degree of conjugation of the Δ^1 double union with the carbonyl double union varies.

Using the Thiele Partial Valence Theory and applying it to two acids,



(I).



(II).

we would predict that, as the unsaturated phenyl ring in acid I is brought into conjugation with the partial valence on the α-carbon (as is the case in Structure II), we would obtain a larger value for the Δ^1 double union. This would be predicted because according to the Thiele view conjugation of the Δ^1 double union has given a weaker acid than initially expected and the partial removal of this conjugation should partly reverse the effect.

The ionization constant of Δ^2-dihydronaphthoic acid-2 (Structure I) is only slightly larger than that of the tetrahydro acid, whereas in the case of Δ^1-dihydronaphthoic acid-1 (Structure II) we find an acid approaching nearly the value for the Δ^2 double union:

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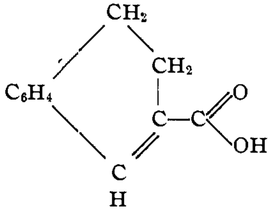
* The double union is here in the Δ^2 position in respect to the carboxyl group, but since Meyer and Jacobson have adopted Baeyer's nomenclature, the writers have also done so.

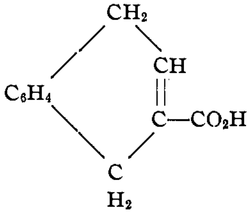
[1] *Z. physik. Chem.*, 3, 174 (1889).

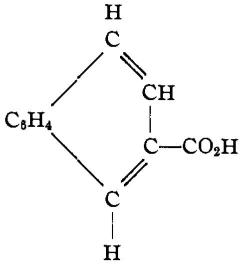
$$\frac{K\ \Delta^1\text{-dihydronaphthoic acid-1}}{K\ ac\text{-tetrahydronaphthoic acid-1}} = \frac{7.90}{4.43} = 1.78$$

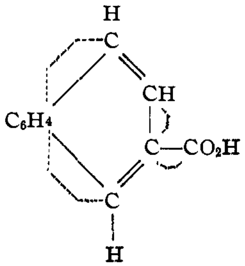
A quantitative measure of the degree of conjugation is, therefore, available if this is found to hold generally.

A comparison of the ionization constants of the two α,β unsaturated dihydro-β-naphthoic acids (Structures III and IV, below) indicates that conjugation on the β-carbon does not seriously affect the value for this constant as is the case when the valence on the α-carbon is conjugated.


(III).


(IV).


(V).


(VI).

Since we now know the ionization constants of both the Δ^1 and Δ^3-dihydro-β-naphthoic acids, we are able to compare the calculated value for β-naphthoic acid with the observed value. The value for the Δ^3 double union as indicated above is 2.33, while the value for the Δ^1 double union is

$$\frac{K\ \text{for}\ \Delta^1\text{-dihydronaphthoic acid-2}}{K\ \text{for}\ ac\text{-tetrahydronaphthoic acid-2}} = \frac{2.91 \times 10^{-5}}{2.47 \times 10^{-5}} = 1.18$$

The calculated value for β-naphthoic acid would therefore be: $2.47 \times 10^{-5} \times 2.33 \times 1.18 = 6.79 \times 10^{-5}$, which agrees well with the observed value (6.90×10^{-5}). The uncertainty[1] connected with the prediction of the ionization constants of disubstituted acids prevents us, however, from using this as an argument to decide between the two structures (V and VI above) for β-naphthoic acid.

Summary.

1. The ionization constant of the new isomeric dihydro-β-naphthoic acid has been determined.

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[1] Wegscheider, *Z. Electrochem.*, 18, 277–81 (1912).

2. The ionization constants of seven other mono-carboxy-naphthalene derivatives have been re-determined.

3. The place influence for a double union in the Δ^2 position in respect to the carboxyl group has been shown to be a constant for the cyclic acids. The dangers of drawing conclusions from the ionization constants of unsaturated aliphatic acids where *cis-trans* isomerism due to the double union is possible, have been emphasized.

4. The place influence for a Δ^1 double union has been shown to vary with the degree of conjugation and it is suggested that a quantitative interpretation of Thiele's Partial Valence Theory may be developed from this standpoint.

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A CONTRIBUTION TO THE THERMAL CHEMISTRY OF PYRIDINE.

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Introduction.

During the past few years considerable work has been done in this laboratory on the solubility of various inorganic salts in pyridine. A number of new compounds having pyridine of crystallization have been discovered, and the equilibria relations of these, together with those of many of the earlier known compounds, have been determined.[1] It was frequently noted that the thermal effect accompanying the formation or the solution of these compounds was very appreciable.

The purpose of the work described in this paper was to measure the heat effects accompanying the act of taking on of pyridine of crystallization. Because of its analogy to the thermal effect accompanying the taking on of water of crystallization, which we call "heat of hydration," we shall, for lack of a better term, refer to the thermal effect under consideration as the "heat of pyridination."

This heat of pyridination was measured in the usual manner, *i. e.*, by determining the heat of solution of the salt first without, and then with, its pyridine of crystallization, the difference between these values yielding the heat of pyridination.

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[1] Kahlenberg and Brewer, *J. Phys. Chem.*, **12**, 282 (1908); Kahlenberg and Wittich, *Ibid.*, **13**, 427 (1909); McBride, *Ibid.*, **14**, 189 (1910); Walton and Judd, THIS JOURNAL, **33**, 1026 (1911); Cotton, M.S. Thesis, University of Wisconsin, 1911; Spero, B.S. Thesis, University of Wisconsin, 1913; Deemer, M.S. Thesis, University of Wisconsin, 1914; Mathews and Benger, *J. Phys. Chem.*, **18**, 264 (1914); Ritter, B.S. Thesis, University of Wisconsin, 1915.