143. *Investigations of the Olefinic Acids. Part VIII. Dissociation Constants.*

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For the purpose mentioned in the preceding paper, the dissociation constants of a number of simple olefinic acids have been redetermined. Many of the acids have recently been isolated in the crystalline condition for the first time (Parts I, V, VI, and VII). The purified acids were finally distilled before use, except those of comparatively high melting point, which were crystallised from both aqueous and non-aqueous solvents. The measurements were carried out as soon as possible after the preparation of the acids, owing to the danger of their contamination on standing by spontaneous polymerisation, oxidation, or isomeric change. All the materials were crystalline solids at low temperatures and had the melting points given in Table I. Δ^γ-n-Hexenoic acid was prepared by two new processes which will shortly be described, the products being the same as that obtained by the original method of Fichter (*Ber.*, 1896, **29**, 2370) and giving an identical dissociation constant. No new determinations have been carried out on acrylic acid (dissociation constant measured by Moureu and Boutaric, *J. Chim. Phys.*, 1920, **18**, 348) and Δ^δ-n-hexenoic acid. Fichter and Langguth's preparation of the latter acid (*Annalen*, 1900, **313**, 371) seems to have been essentially free from the only likely impurity (the Δ^γ-isomeride), as its hydrobromide yielded no γ-hexolactone on hydrolysis. We are, however, confirming Fichter's figure for the constant of this acid.

Summary of Results.—The measurements and calculations involved in the determination of the dissociation constants are described in a later section. The figures in Table I are true dissociation constants, accurate to 1%. The values for acetic and benzoic acids have also been determined by the same method, so that direct comparison is possible between these results and those of other workers.

Only β-methyl-Δ^α-pentenoic acid has been examined in both stereoisomeric forms. The other Δ^α-unsaturated acids may be assumed to be the *trans*-isomerides, as they are prepared by a method which in the case of crotonic acid gives the acid of m. p. 72°, now known with certainty to be the *trans*-modification.* The acids with more distant double bonds are, without exception, only known in one form, and it is in any case doubtful whether stereoisomerides about such double bonds would differ appreciably in their dissociation constants.

Because of possible complications in the interpretation of the results, no acids have been studied with alkyl substituents on the carbon atoms on the same side of the double bond as the carboxyl group, but it is hoped to study them shortly.

Comparison with Previous Results.—The older values determined by Ostwald (*Z. physikal. Chem.*, 1889, **3**, 369) and by Fichter and Pfister (*Annalen*, 1904, **334**, 201) and Fichter and Gisiger (*Ber.*, 1909, **42**, 4707) were calculated from the Ostwald dilution law, whereas the values in Table I are corrected on the basis of the Debye–Hückel–Onsager equation. Calculation on the basis of the simple dilution law from our experimental figures gives results more variable and some 2% higher than the corrected values.

* It is possible that the γ-methyl-Δ^α-pentenoic acid used was not a stereochemical individual (J., 1932, 124).

TABLE I.

| Acid.	Formula.	M. p. (corr.).	Method of prepn.	$K_{25°} \times 10^5$.
Acetic	—	—	—	1·78
Benzoic	—	—	—	6·46
(Acrylic	$CH_2{:}CH{\cdot}CO_2H$	12·3°	(1)	5·6)
Crotonic	$CHMe{:}CH{\cdot}CO_2H$	72	(2)	2·03
Vinylacetic	$CH_2{:}CH{\cdot}CH_2{\cdot}CO_2H$	—35	(3)	4·48
Δ^α-n-Pentenoic	$CHEt{:}CH{\cdot}CO_2H$	9·5	(4)	2·02
Δ^β-n-Pentenoic	$CHMe{:}CH{\cdot}CH_2{\cdot}CO_2H$	1·5	(3)	3·11
Δ^γ-n-Pentenoic	$CH_2{:}CH{\cdot}[CH_2]_2{\cdot}CO_2H$	—22·5	(5)	2·10
$\beta\beta$-Dimethylacrylic	$CMe_2{:}CH{\cdot}CO_2H$	69	(6)	0·76
Δ^α-n-Hexenoic	$CH_2Et{\cdot}CH{:}CH{\cdot}CO_2H$	33	(7)	1·98
Δ^β-n-Hexenoic	$CHEt{:}CH{\cdot}CH_2{\cdot}CO_2H$	12	(7), (3)	3·05
Δ^γ-n-Hexenoic	$CHMe{:}CH{\cdot}[CH_2]_2{\cdot}CO_2H$	1	*v.s.*	1·91
(Δ^δ-n-Hexenoic	$CH_2{:}CH{\cdot}[CH_2]_3{\cdot}CO_2H$	—	(8)	1·90)
γ-Methyl-Δ^α-pentenoic	$CHMe_2{\cdot}CH{:}CH{\cdot}CO_2H$	—32	(9)	1·99
γ-Methyl-Δ^β-pentenoic	$CMe_2{:}CH{\cdot}CH_2{\cdot}CO_2H$	— 2	(9), (4)	2·51
trans-β-Methyl-Δ^α-pentenoic	$CH_2Me{\cdot}CMe{:}CH{\cdot}CO_2H$	47	(10)	0·74
cis-β-Methyl-Δ^α-pentenoic	$CH_2Me{\cdot}CMe{:}CH{\cdot}CO_2H$	12	(10)	0·71
δ-Methyl-Δ^γ-hexenoic	$CMe_2{:}CH{\cdot}[CH_2]_2{\cdot}CO_2H$	—33	(5)	1·59

References to preparative methods : (1) Moureu and Boutaric, *loc. cit.* (2) Letch and Linstead, J., 1932, 443. (3) Linstead, Noble, and Boorman, preceding paper. (4) Boorman, Linstead, and Rydon, this vol., p. 568. (5) Linstead and Rydon, this vol., p. 580. (6) Barbier and Léser, *Bull. Soc. chim.*, 1905, **33**, 815. (7) Boxer and Linstead, J., 1931, 740. (8) Fichter, *loc. cit.* (9) Linstead, J., 1932, 115. (10) J. M. Wright, unpublished work.

The recorded data are in fair to good agreement with the new figures (added in parentheses) for the following acids : crotonic, 2·04 (2·03) ; Δ^γ-pentenoic, 2·09 (2·10) ; Δ^α-hexenoic, 1·89 (1·98) ; Δ^γ-hexenoic, 1·74 (1·91) ; *trans*-β-methyl-Δ^α-pentenoic, 0·73 (0·74). The older value for vinylacetic acid, 3·83 (Fichter and Pfister, *loc. cit.*), is much less than that now found (4·48), and the difference must be attributed to the presence of some less conducting impurity, probably crotonic acid, in the old material. The value found by Fichter and Pfister for Δ^β-n-hexenoic acid (2·64 as against 3·05) is undoubtedly low owing to the presence of an isomeride, either the Δ^α- or the Δ^γ-acid according to the method of preparation (which is not specifically stated, although it was probably the reduction of sorbic acid). More surprising are the appreciable divergences in the figures for the Δ^α- and Δ^β-n-pentenoic acids, which are comparatively readily obtained pure, and for which Fichter and Pfister give 1·48 (2·02) and 3·35 (3·11) respectively. The other constants have not previously been determined.

" International Critical Tables " (1929, VI, 269) record values for $\beta\beta$-dimethylacrylic acid of $K \times 10^4 = 2\cdot00$ and 2·20, from determinations by Walker and by Pfaff, quoted by Perkin (J., 1896, **69**, 1461). These are based on a textual error in Perkin's paper and are actually intended for $\beta\beta$-dimethylglutaric acid; the word " *acrylic* " on p. 1461, line 10 of this paper should read " *glutaric.*" This is clear from the context and from the identity of the values recorded with those found for $\beta\beta$-dimethylglutaric acid by the same workers (*Annalen*, 1896, **292**, 146).

DISCUSSION.

The dissociation of a carboxylic acid in water in terms of the forward reaction may be represented by the expression

$$R{-}C{\bigotimes_{O-H}^{O}} + H_2O \longrightarrow R{-}C{\bigotimes_{O}^{O}}_\ominus + H_3\overset{\oplus}{O}$$
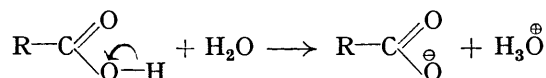
(cf. Allan, Oxford, Robinson, and Smith, J., 1926, 401). As is generally recognised, it is assisted by any constitutional factor which tends to bring the covalency electrons of the O–H link more under the control of the oxygen atom, and thus enable a water molecule to detach a proton. Substitution of halogen in the paraffin chain (R) provides an example of such a factor, and the comparatively high acidity of the aliphatic chloro-acids can be attributed to the presence of the $\overset{-}{Cl}{\longleftarrow}\overset{+}{C}$ dipole.

Olefins have almost negligible polar moments, and the olefinic acids may be presumed to contain no permanent dipole in the aliphatic chain similar to that present in the chloro-acids. On the other hand, if the double bond is polarisable, there will be in the molecule a latent source of electrical adjustment which at the demand of the attacking reagent (water) will function in such a manner as to facilitate the reaction. To do this, the double bond will polarise so as to present a positive face to the carboxyl group, the tendency of this group to acquire a negative charge, and therefore the dissociation, thus being increased :

$$a \qquad\qquad\qquad\qquad\qquad b$$
$$\overset{\frown}{C}\!=\!C\ \ \delta^{+} \mathrel{\rightsquigarrow} \ \ \delta^{-}\overset{\frown}{CO\cdot O}\!\!-\!\!H$$
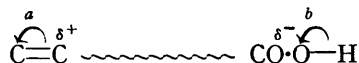
The greater the capacity for the ethylenic polarisation represented by *a*, the greater will be the dissociation inaugurated by the process *b* and followed by the attack of a molecule of water.

The recorded constants of the saturated acids from propionic to *iso*hexoic acid may be taken as $K_{25°} \times 10^5 = 1.5 \pm 0.2$, and the dissociation constant of a fatty acid higher than acetic may be regarded as practically independent of the length of the chain and the alkyl substitution (with the apparent exception of those acids in which the α-carbon atom is heavily substituted, such as trimethylacetic acid; $K_{25°} \times 10^5 = 0.98$). Compared with this figure, the results in Table I show that the unsaturated acids are either as strong as or stronger than saturated acids with the same carbon skeleton, with the single exception of ββ-dialkylacrylic acids. These are discussed later.

The polar effect of the double bond, like that of a halogen atom, is almost completely eliminated when the bond is removed by two or more methylene groups from the carboxyl, and the dissociation constants of unsaturated acids approach those of the corresponding saturated acids as the double bond recedes from the carboxyl group. This is shown in Table II, where the corresponding figures for the recession of a bromine atom (Ostwald, *loc. cit.*, p. 170; Lichty, *Annalen*, 1901, **319**, 369) are given for comparison.

TABLE II.

Dissociation Constants ($K_{25°} \times 10^5$) *of* $R\cdot[CH_2]_x\cdot CO_2H$.

x.	R = CH₂:CH.	R = CH₂Br.	*x*.	R = CH₂:CH.	R = CH₂Br.
0 (Δ^α)	5·6	138	2 (Δ^γ)	2·10	2·6
1 (Δ^β)	4·48	9·8	3 (Δ^δ)	1·91	1·9

The question whether there is a small permanent residual effect, or whether the remaining increment would disappear with further recession of the group R, cannot be decided from the available figures.

Alkyl Substitution.—The effect of distant alkyl substitution about the double bond * on the dissociation constant of an unsaturated acid provides convincing evidence of the polarisability of the double bond. Recent measurements of polar moments have confirmed Lucas's conception that the methyl group exercises less restraint over its covalency electrons than does hydrogen (represented by the sign $CH_3 \longrightarrow$). On the present hypothesis, therefore, distant alkylation substitution should inhibit the polarisation *a* in comparison with that of the unsubstituted acids, and to some extent stop the accommodating effect of the double bond on the dissociation of the carboxyl, thus :

$$a$$
$$CH_3 \!\longrightarrow\! \overset{\frown}{C}\!=\!C \mathrel{\rightsquigarrow} CO\cdot OH$$
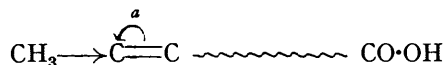
In any series, $CH_2\!:\!CH\cdot[CH_2]_x\cdot CO_2H$, $CHR\!:\!CH\cdot[CH_2]_x\cdot CO_2H$, $CR_2\!:\!CH\cdot[CH_2]_x\cdot CO_2H$, the dissociation constant should therefore fall with the substitution. The interpretation of the results is simplified by the fact, already mentioned, that a similar substitution in the corresponding saturated acids produces no appreciable effect.

* Alkyl substitution on the ethylene carbon atom further from the carboxyl group is termed " distant "; that on the near carbon atom is termed " proximate." It is convenient also to apply these terms to the carbon atoms themselves.

It is to be expected also that the differences caused by substitution in this way should be greater, the nearer the double bond is to the carboxyl group.

In both these respects the demands of the hypothesis are fully verified by the experimental facts, summarised in Table III.

TABLE III.

The Effect of Distant Alkyl Substitution on the Dissociation Constants of Olefinic Acids, $R^1R^2C:CH \cdot [CH_2]_x \cdot CO_2H$.

Distant substituents.		Dissociation constants.		
R^1.	R^2.	*trans*-Δ^α-Acids $(x = 0)$.	Δ^β-Acids $(x = 1)$.	Δ^γ-Acids $(x = 2)$.
H	H	5·6	4·48	2·10
H	Me	2·03	3·11	1·91
H	Et	2·02	3·05	—
H	Pr$^\alpha$	1·98	—	—
H	Pr$^\beta$	1·99	—	—
Me	Me	0·76	2·51	1·59
Me	Et	0·74	—	—

These figures show that, for a given position of the double bond, the dissociation constant is determined by the *order* but not by the actual *nature* of the alkyl substitution.

It is clear from these results and from those of parallel investigations described in this series that in examining the effect of a double bond on a reaction it is necessary to recognise the existence of different *types* of ethylenic double bond; *e.g.*, in estimating the effect of recession of the double bond on the dissociation constant, as was done in Table II, a true comparison could only be made between acids of the same type, in this case those containing the vinyl group.

The Abnormality of Δ^α-*Double Bonds.*—The dissociation constant of a halogenated fatty acid (see, *e.g.*, Table II) increases rapidly as the substituent approaches the carboxyl group, and is multiplied tenfold when the halogen atom passes from the β- to the α-carbon atom. The vinyl double bond produces a comparable effect on the dissociation constant on moving from the γ- to the β-carbon atom, but no such large increase on passing to the α-carbon atom : acrylic acid is only slightly stronger than vinylacetic acid. Other types of double bond even produce a fall in the dissociation constant when they pass from the βγ- to the αβ-position. It is clear, therefore, that a disturbing factor comes into play.

The nature of this was foreseen by Robinson (*loc. cit.*), who suggested that the conjugation of the double bond with the carboxyl group was " a factor tending to weaken an acid."

The process at work here may be represented as follows :
$$C{=}C{-}C{=}O$$
$$O{-}H,$$
the "katio-enoid" polarisation of the conjugated system (from left to right in the formula) acting so as to lessen the capacity of the second oxygen atom to acquire the negative charge.

The exact effect of this on the dissociation constant will depend upon the type of the Δ^α-double bond. It may be suggested that the effect of conjugation in acrylic acid is to depress the constant from $K \times 10^5 =$ about 50, which is indicated by analogy with the α-halogenated acids (Table II), to the observed value of 5·6. A similar argument explains why crotonic acid and substances of similar type are weaker than their Δ^β-isomerides, as noted by Fichter (*loc. cit.*), and why, in the extreme case, ββ-dialkylacrylic acids are actually weaker than the corresponding saturated acids. The normal enhancement of dissociation is so weak with the last type of double bond that the effect of conjugation overpowers it.

The dissociation of the unsaturated acids dealt with in this paper is therefore believed to be influenced by (i) a general enhancement due to the presence of the double bond, which diminishes with its recession from the carboxyl group and is modified by alkyl substitution, and (ii) a special depression in Δ^α-acids due to conjugation. The available data do not clearly reveal the operation of any other constitutional factors.

Brief reference may be made to two conceptions on this subject which appear to be mistaken. First, there seems no justification for attaching any particular significance to

the alternation of dissociation constant as the double bond recedes along the chain (Flür-scheim, *J.*, 1909, **95**, 721). The alternation which is observed, for example, in the Δ^{α}-, Δ^{β}-, and Δ^{γ}-*n*-hexenoic acids arises accidentally from the operation of the conjugational factor in the case of the Δ^{α}-acid and is not found after these first three members. Secondly, the new results finally refute the idea that when unsaturated acids undergo isomeric change, the *weaker* of the two possible isomerides is formed (Derick, *J. Amer. Chem. Soc.*, 1910, **32**, 1333). This is disproved by consideration of the γ-methylpentenoic acids, the Δ^{α}-form of which ($K \times 10^5 = 1.99$) passes to the extent of 78% into the Δ^{β}-form ($K \times 10^5 = 2.51$).

Measurement and Calculation of the Dissociation Constants.

Measurement of Conductivities.—The measurement of the specific conductivities of the aqueous solutions of the acids and sodium salts, and the preparation of the sodium salts, were carried out in a similar manner to that already described (Ives and Riley, *J.*, 1931, 1998; Ives, Linstead, and Riley, *J.*, 1932, 1093). The composition of the sodium salts was checked by analysis.

Solvent Correction.—The specific conductivity of the water was 0.3—0.5×10^{-6} reciprocal ohm. No correction was applied to the acid solutions, on the assumption that the main impurity in the water was carbonic acid (Wynne-Jones, *J. Physical Chem.*, 1927, **31**, 1647), which was justified by a series of careful measurements on the same acid in waters of different specific conductivities. The best concordance was obtained when no correction was applied.

The normal water correction was applied to the results for the sodium salts. Davies (*Trans. Faraday Soc.*, 1932, **28**, 607) has pointed out that such a procedure with salts of weak acids is likely to lead to serious errors in the determination of mobility values. More-over, concentrated solutions of the sodium salts were found to be slightly alkaline, indicating hydrolysis.

To estimate the extent of these errors, the following calculations were made. The equation $[OH'] + [HCO_3'] + [A'] = [H^{\cdot}] + [Na^{\cdot}]$, which denotes the electroneutrality of the solution and controls the degree of hydrolysis of the salt, can be expressed in terms of $H^{\cdot}$ and known quantities :

$$\frac{K_w}{[H^{\cdot}]} + \frac{K_c m}{[H^{\cdot}] + K_c} + \frac{K_a M}{[H^{\cdot}] + K_a} = [H^{\cdot}] + M$$

where K_w is the ionic product for water, $= 10^{-14}$; $K_c =$ the primary dissociation constant of $H_2CO_3 = 3.50 \times 10^{-7}$ (Kendall, *J. Amer. Chem. Soc.*, 1916, **38**, 1480); $K_a =$ the dissociation constant of the acid HA; $m =$ the *total* concentration of H_2CO_3, which is determined from the conductivity of the water used as solvent; and $M =$ the *total* concentration of sodium salt. This equation was solved by the method of successive approximations, and the true solvent correction determined from the mobilities and concentrations of the respective ionic species.

For dimethylacrylic acid, which, being one of the weakest acids of the series, would have shown the largest error, and for acetic acid the true correction has been found to be less than the normal correction, which at first seems rather surprising. It must be remembered, however, that the initial conductivity of the water used as solvent is almost entirely due to hydrogen ions, *i.e.*, the water is on the acid side of neutrality. These hydrogen ions are almost entirely removed by the hydrolysis, together with some acid anions, and the increase in the concentration of the hydroxyl ions is too small to compensate for this.

For sodium dimethylacrylate, the true correction varied from 0.21 to 0.08×10^{-6} reciprocal ohm, according to the concentration of the sodium salt, whereas the normal conductivity correction was 0.51×10^{-6}. This alteration in the correction had the effect of improving the concordance of the mobility values. The results for sodium dimethyl-acrylate are in Table IV, and indicate the accuracy obtained in the other measurements. Λ indicates the value of the equivalent conductivity obtained when the normal correction is applied, and Λ' when the true correction is applied. Λ_0 and Λ_0' are the relevant values of the equivalent conductivity at zero concentration.

TABLE IV.

$10^3 C$ (mols./l.).	Λ.	Λ'.	Λ_0.	Λ_0'.	$10^3 C$ (mols./l.).	Λ.	Λ'.	Λ_0.	Λ_0'.
6·5170	76·35	76·40	82·8	82·8	1·9202	78·87	79·09	82·3	82·6
5·6141	76·90	76·95	82·8	82·9	1·6567	79·28	79·54	82·5	82·8
5·0201	76·93	76·99	82·6	82·6	0·9292	79·96	80·45	82·4	82·9
3·9023	77·44	77·53	82·4	82·5	0·7614	79·98	80·58	82·2	82·8
3·8311	77·83	77·92	82·7	82·8			Mean	82·5	82·75
2·6133	78·56	78·71	82·6	82·8					

Whence values of Λ_0 of the acid $= 380\cdot15 \quad 380\cdot40$

The mobilities of the sodium and hydrogen ions have been taken as 51·4 and 349·05 respectively (Ferguson and Vogel, *Phil. Mag.*, 1927, **4**, 233, 300).

The difference on the values of Λ_0 for the acid represents a change in the dissociation constant from 0·767 to 0·766 $\times$ 10^{-5}, which is well within the experimental error. The change in the case of acetic acid was even less.

All the sodium salts studied gave constant values for Λ_0' over the concentration range indicated in Table IV. This extends to higher concentrations than is customary in the application of the Onsager equation, but in our experiments deviations from constancy only appeared at about 8×10^{-3} mol. per litre.

These results indicate that little error is likely to arise from this source, providing that measurements are made over a considerable range of concentrations of sodium salt and that good conductivity water is used. Even with an acid as weak as dimethylacrylic acid, the true correction is less than the normal correction. With weaker acids the increased hydrolysis would render the solution of the sodium salt more alkaline and the true correction would approach and finally exceed the normal correction. It is probable, therefore, that such errors become serious only in the case of sodium salts of dibasic acids, where the hydrolysis occurs to a much greater extent (Ives, Linstead, and Riley, *loc. cit.*).

Mobilities of Isomeric Ions.—Mobility determinations were carried out to determine whether the ions of isomeric acids of this type have the same mobility. Differences were observed which, whilst insufficient to cause any significant variation of K, were greater than the experimental error, but were not sufficiently precise for definite conclusions to be drawn. The method of weight dilution employed was not suitable for such an investigation, since exposure of the solutions to the air and consequent slight contamination were unavoidable. The results for sodium dimethylacrylate recorded in Table IV were of two independent series of measurements and showed that the accuracy was sufficient for the purposes of this paper.

Calculation of Mobilities and Dissociation Constants.—Mobilities were calculated from the sodium salt data by substituting the experimental figures for equivalent conductivity in the Onsager equation (Onsager, *Trans. Faraday Soc.*, 1927, **23**, 341), excellent agreement with the theoretical slope of the equation being obtained (cf. Table IV).

True dissociation constants were calculated, corrections for mobility variations with concentration being applied to the ionised part of the solute by means of the Onsager equation (*loc. cit.*), and for activity variation by means of the Debye–Hückel equation (Davies, *Phil. Mag.*, 1927, **4**, 244), no assumption being made as to the value of the constant A in the equation (see Davies, " Conductivity of Solutions," 1930, pp. 86—90).

Until recently it was thought that the value 0·5065 ascribed by the Debye–Hückel equation to this constant was erroneous, and much experimental evidence was advanced in favour of the value 0·39 or 0·40 (Noyes, *J. Amer. Chem. Soc.*, 1924, **46**, 1080, 1098; Randall and Vanselow, *ibid.*, p. 2418; Nonhebel, *Phil. Mag.*, 1926, **2**, 1085; Davies, *ibid.*, 1927, **4**, 244; Blayden and Davies, J., 1930, 949) or of a value varying with the electrolyte (Davies, J., 1930, 2410, 2421).

The recent papers of MacInnes and Shedlovsky (*J. Amer. Chem. Soc.*, 1932, **54**, 1429), Hall (*ibid.*, p. 831), LaMer and Goldman (*ibid.*, 1929, **51**, 2632), and Davies (*ibid.*, 1932, **54**, 1698) have provided very strong support for the Debye–Hückel theory, and it is indicated that the equation is correct as a limiting equation in very dilute solutions. In stronger solutions so-called " medium effects " and viscosity (see Davies, *J. Amer. Chem. Soc.*, 1932, **54**, 3776) due to the increasing concentration of un-ionised solute cause a divergence.

TABLE V.

$10^3 C$ (mols./l.).	Λ.	$K \times 10^5$.	$K' \times 10^5$.

trans-*Crotonic acid*.

Λ_0 from Na salt = 382·05.

11·855	15·69	2·09	2·02
5·7197	22·34	2·08	2·03
2·2650	34·90	2·08	2·04
1·1664	47·57	2·07	2·03
0·3735	79·65	2·05	2·03

Mean of 17 determinations 2·03

Δ^α-n-*Pentenoic acid*.

Λ_0 from Na salt = 379·75.

14·252	14·12	2·05	2·01
6·9606	20·09	2·06	2·03
2·9430	30·36	2·04	2·02
1·0129	50·11	2·03	2·02
0·1647	112·0	2·03	2·02

Mean of 14 determinations 2·02

Δ^γ-n-*Pentenoic acid*.

Λ_0 = Mean of values for Δ^α- and Δ^β-acids = 380·15.

10·428	17·11	2·15	2·10
4·9235	24·28	2·14	2·10
1·7914	39·34	2·14	2·11
0·7835	57·75	2·13	2·11
0·3227	85·68	2·12	2·10

Mean of 13 determinations 2·10

Δ^α-n-*Hexenoic acid*.

Λ_0 from Na salt = 377·85.

8·1482	18·30	2·01	1·97
3·3387	28·20	2·01	1·98
1·7130	38·72	2·00	1·98
0·9354	51·34	2·00	1·98
0·2739	89·08	1·99	1·97

Mean of 15 determinations 1·98

Δ^γ-n-*Hexenoic acid*.

Λ_0 = Mean of values for Δ^α- and Δ^β-acids = 377·60.

10·152	16·23	1·96	1·90
5·7510	21·40	1·96	1·91
3·0800	28·87	1·95	1·91
1·0350	48·20	1·93	1·90
0·5702	63·22	1·92	1·90

Mean of 12 determinations 1·91

γ-*Methyl*-Δ^β-*pentenoic acid*.

Λ_0 assumed the same as for the Δ^α-acid = 378·45.
First sample, mean of 13 determinations 2·41.
Second sample, melting 2° higher.

13·4038	16·16	2·55	2·51
9·9367	18·71	2·56	2·51
7·0513	22·11	2·56	2·52
3·2769	31·92	2·55	2·51
2·1225	39·19	2·54	2·51

Mean of 6 determinations 2·51

cis-β-*Methyl*-Δ^α-*pentenoic acid*.

Λ_0 from Na salt = 379·05.

11·847	9·278	0·728	0·715
4·0520	15·68	0·723	0·714
2·8483	18·57	0·720	0·710
1·7266	23·54	0·710	0·703
0·6116	38·60	0·706	0·701

Mean of 11 determinations 0·710

Vinylacetic acid.

Λ_0 assumed the same as for crotonic acid = 382·05.

10·470	24·48	4·59	4·48
5·8346	32·39	4·58	4·49
3·1872	43·09	4·57	4·49
1·7564	56·75	4·55	4·48
0·4800	100·7	4·53	4·49

Mean of 14 determinations 4·48

Δ^β-n-*Pentenoic acid*.

Λ_0 from Na salt = 380·55.

13·446	18·14	3·21	3·12
7·7378	23·67	3·19	3·12
2·7533	38·60	3·15	3·09
0·8233	67·72	3·17	3·13
0·1510	138·3	3·13	3·10

Mean of 11 determinations 3·11

$\beta\beta$-*Dimethylacrylic acid*.

Λ_0 from Na salt = 380·15.

13·431	8·990	0·769	0·757
6·8079	12·58	0·771	0·761
2·1233	22·22	0·770	0·763
1·1876	29·35	0·767	0·761
0·3820	50·05	0·763	0·758

Mean of 16 determinations 0·759

Δ^β-n-*Hexenoic acid*.

Λ_0 from Na salt = 377·35.

12·8055	18·12	3·10	3·04
5·6831	26·88	3·10	3·06
2·6199	38·86	3·10	3·06
1·0089	60·44	3·08	3·05
0·2664	108·1	3·06	3·05

Mean of 15 determinations 3·05

γ-*Methyl*-Δ^α-*pentenoic acid*.

Λ_0 from Na salt = 378·45.

9·8277	16·82	2·03	2·00
4·5969	24·34	2·03	2·00
2·4596	32·77	2·02	1·99
1·2746	44·81	2·03	2·01
0·3322	81·94	1·99	1·98

Mean of 13 determinations 1·99

trans-β-*Methyl*-Δ^α-*pentenoic acid*.

Λ_0 from Na salt = 380·15.

12·516	9·021	0·745	0·734
5·2548	14·06	0·746	0·738
2·5160	20·11	0·743	0·737
1·1632	29·08	0·737	0·731
0·4864	44·28	0·747	0·741

Mean of 16 determinations 0·736

δ-*Methyl*-Δ^γ-*hexenoic acid*.

Λ_0 from Na salt = 376·25.

9·4878	15·18	1·61	1·58
5·0036	20·76	1·61	1·59
2·6643	28·13	1·61	1·59
1·1494	41·93	1·61	1·59
0·7137	52·30	1·60	1·59

Mean of 12 determinations 1·59

The result is that the experimental relationship between log (C_i^2/C_u) and $\sqrt{C_i}$ (see Davies, *Phil. Mag.*, 1927, **4**, 244) is no longer linear, but a curve of decreasing gradient towards the region of stronger solutions. This curvature is not apparent except in measurements of considerable accuracy; hence the misconception as to the value of the constant A has arisen.

In the case of the acids here studied, the curvature was apparent in some of the measurements, but in general, the precision of the results and the possible presence of disturbing factors such as polymerisation did not allow a strictly accurate extrapolation to be carried out.

In all cases, therefore, the best straight line was drawn through the experimental points, and the dissociation constant calculated on this basis. The error due to this procedure was about 0·5%, well within the experimental error.

In order to provide a check on the values of the constants obtained, and to bring them into line with other values published in the literature, the constants for pure acetic and benzoic acids were determined by the same general methods : they are given below, together with the most trustworthy of those of other workers.

Acetic acid : Found, $K = 1·78 \times 10^{-5}$ (mean of 11 determinations). MacInnes (*J. Amer. Chem. Soc.*, 1926, **48**, 2068), 1·74—1·78; Davies (*Phil. Mag.*, 1927, **4**, 249), 1·785; Harned and Owen (*J. Amer. Chem. Soc.*, 1930, **52**, 5079), 1·75; Harned and Ehlers (*ibid.*, 1932, **54**, 1350), 1·754; MacInnes and Shedlovsky (*ibid.*, p. 1429), 1·752; Jeffery and Vogel (*J.*, 1932, 2829), 1·776.

Benzoic acid : Found, $K = 6·46 \times 10^{-5}$ (mean of 6 determinations). White and Jones (*Amer. Chem. J.*, 1910, 197), 6·38—6·72; Larsson (*Z. anorg. Chem.*, 1926, **155**, 247), 6·5; Kirschman, Wingfield, and Lucas (*J. Amer. Chem. Soc.*, 1930, **52**, 23), 6·68 $\pm$ 0·25; Kolthoff and Bosch (*J. Physical Chem.*, 1932, **36**, 1695), 6·7.

RESULTS.

The results are in Table V, together with the mean of the total number of determinations made in each case. Some of the experimental values of equivalent conductance have been included so that calculations using other mobility values may be carried out if desired. K is the dissociation constant calculated from the ordinary Ostwald dilution law, and K' is the true dissociation constant obtained as described above.

The absolute accuracy of the results has been assessed, account being taken of the possible error in the mobility values, and is of the order of 1·0%.