PHYSICAL CONSTANTS OF SOME SUBSTITUTED MALONIC ACIDS

THE PHYSICAL CONSTANTS OF SOME SUBSTITUTED MALONIC ACIDS,

WITH SPECIAL REGARD TO THE INFLUENCE OF ALKYL SUBSTITUENTS ON THE ELECTRICAL CONDUCTIVITY OF MALONIC ACID.

Thesis Presented to the Committee on
Graduate Studies of McGill University
for the Degree of Master of Science,

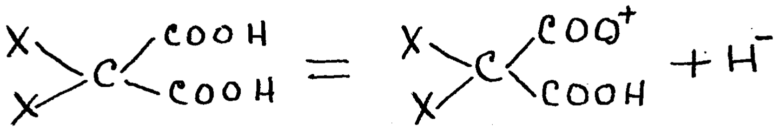
By

W. BUELL MELDRUM, B. A.

APRIL, 1910.

The Physical Constants of Some Substituted Malonic Acids.

The first determinations of the electrical conductivity of dibasic organic acids were made by Ostwald*in 1888,who examined among others a few of the simpler alkyl substituted malonic acids with the purpose of testing his dilution law for binary electrlytes it having previously been found that weak dibasic organic acids dissociate into two ions and not into three:



$$\mathrm{X_2C(COOH)_2 = X_2C(COO^+)(COOH) + H^-}$$

?

Malonic ,methyl malonic,ethyl malonic and di-methyl malonic acids were the only ones of the malonic series of acids which were studied by him.

Ostwald's research was followed by another by Bethmann in 1890,who made a special study of dibasic organic acids.He determined the electrical conductivity for each of the first nine acids of the oxalic series and showed that starting with oxalic acid the dissociation constant decreased,rapidly at first,then more slowly,with the increase of the distance between the carboxyl groups.He repeated the measurements of Ostwald on the malonic acids and added two more to his list:propyl malonic and iso-propyl malonic acids.His determinations for the succinic acids were more extensive, and for them he showed that the introduction of an alkyl group into succinic acid caused an increase in the value of the dissociation constant, the ethyl and the methyl groups having the same effects, but two ethyl groups substituted for the two hydrogen atoms attached to one carbon atom having a greater effect than two methyl groups similarly substituted. Although not considered at that time, such a difference in behaviour indicates unmistakably some condition akin to steric hindrance in the molecule. Bethmann's results show the reverse property for malonic acids, the constant decreasing with the substitution of alkyl radicals.

Walden*, in the year following the publication of the results of Bethmann's research, took up the same branch of the work, but limited himself largely to substituted malonic and succinic acids, studying the properties of the phenyl as well as the alkyl derivatives. As his results are the most complete so far obtainable, a table is given below, which includes also the results of Ostwald's and of Bethmann's results for the purpose of comparison.

	Walden.		Bethmann.	Ostwald.
Acid.	M.P.	K.	K.	K.
Malonic.	131-132	.163	.171	.158
Methyl Malonic.	128	.086	086	.087
Ethyl Malonic.	110-112	.127	---	.127
Di-Methyl Malonic.	---	.076	---	.077
N-Propyl Malonic.	94-96	----	.113	---
Iso-Propyl Malonic.	87-90	.127	.127	---
N-Butyl Malonic.	102	.103	---	---
Iso-Butyl Malonic.	107	.090	---	---
Di-Ethyl Malonic.	120-121	.740	---	---
Methyl Ethyl Malonic.	118-119	.161	---	---

Walden points out that when analogous acids are compared the the dissociation constants increase with the increase of molecular weight.

Acid.	Molecular Weight.	K.
Di-Methyl Malonic.	132	.076
Ethyl Methyl Malonic.	146	.161
Di-Ethyl Malonic.	160	.740

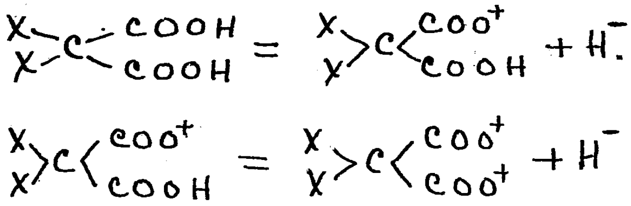
Results show that succinic acids have the same property,as has been already referred to in the discussion of Bethmann's research.

In 1892, James Walker published a paper on "The Dissociation Constants of Organic Acids"*, which included the results previously obtained for some of the alkyl substituted malonic acids together with his own results on the acid esters of the same series. The effect of substituting the ethyl radical for the hydrogen atom of one of the carboxyl groups was found to decrease the value of the dissociation constant by approximately one-half.

Walker advances a general theory regarding dibasic organic acids explanatory of the decrease of dissociation accompanying the increase of distance between the carboxyl groups. "It is owing", he says, "to the effect of one carboxyl group on another. Carboxyl, in virtue of its acid character, increases the dissociation of the hydrogen of the carboxyl group contained in the same molecule as itself, and this increase is greater the more nearly the carboxyl groups occur together in the molecule."

Geometrical isomerism problems may be attacked with some success from this standpoint. The fact that the dissociation constant of maleic acid is twelve times that of fumaric acid indicates closer approximation of the carboxyl groups in the former than in the latter, a conclusion which agrees well with the behaviour of the two on heating Lehfeldt* also refers to this as the probable explanation and suggests that, instead of the distance between the two carboxyl groups increasing, the substituted alkyl groups possibly interfere, in virtue of their position in the molecule, in the inter-action, electrical attraction or repulsion, between the two carboxyl groups. The decrease in the dissociation constant might also be caused by the alkyl substituted group occupying a larger volume within the molecule than the hydrogen atom it displaces, thus actually increasing the distance between the carboxyl groups.

W.A.Smith* has recently further examined the manner in which organic dibasic acids dissociate. From his results he draws the important conclusion that as the dissociation constant for the breaking up of the molecule of malonic acid into the hydrogen and the alkyl acid malonyl ions increases, the dissociation constant for the dissociation of the acid malonyl ion into the ions hydrion and normal malonyl ion decreases.



$$\begin{matrix}X\\X\end{matrix}\!>C<\!\begin{matrix}COOH\\COOH\end{matrix} = \begin{matrix}X\\X\end{matrix}\!>C<\!\begin{matrix}COO^{+}\\COOH\end{matrix} + H^{-}.$$

$$\begin{matrix}X\\X\end{matrix}\!>C<\!\begin{matrix}COO^{+}\\COOH\end{matrix} = \begin{matrix}X\\X\end{matrix}\!>C<\!\begin{matrix}COO^{+}\\COO^{+}\end{matrix} + H^{-}$$

Wagscheider* has done work along similar lines and his results show that the stronger the acid, as shown by its affinity constant, the smaller the dilution at which dibasic dissociation becomes marked.

Lehfeldt*points out that iso-alkyl groups have effects which are different from those of normal groups, a statement which is borne out by the few measurements so far made in the case of malonic acids, though the extent of this difference has not yet been shown. Bone and Sprankling*state that the dissociation constants of normal substituted derivatives of succinic acids increase with an increase in the number of carbon atoms in the molecule. By analogy malonic acid derivatives would be expected to show similar effects though this fact remains to be proven.

Additional evidence in support of the theory that the position of the alkyl groups in the malonic acid molecule to a very large extent determines any variations in the properties due to them, such variations therefore being due not wholly to the peculiarities in the nature of the substituting groups, was furnished by Reicher* in 1885, who measured the rate of hydrolysis of certain esters. He decided that the rate of the reaction depended partly on the nature of the alkyl radical and partly on the nature of the acid radical. The hydrolysis constants for the alkyl groups, the lower members only of which were studied, fall with the increase of molecular weight, with the one exception that iso-butyl acetate was more difficult to hydrolyse than was iso-amyl acetate, indicating that the accumulation of substituents near the hydroxyl group in the molecule of the iso-butyl acetate exerts hindering effect upon the reaction. Acids of the monobasic aliphatic series show a similar influence in the hydrolysis of their ethyl esters.*

Hjelt* made a decided advance in the same direction when he found that in the case of alkyl substituted malonic acids, the ethyl, propyl and iso-butyl derivatives of malonic ester are easily hydrolysed, while the iso-propyl compound is much more slowly changed. The hydrolsis of di-alkyl malonic esters is an extremely slow operation in many cases. The following are examples of his results:—

Ester.	Time.	% Hydrolysed.
Malonic.	160 Min.	61.4
Ethyl Malonic.	——	62.2
Propyl Malonic.	——	60.4
Iso-Propyl Malonic.	——	46.0
Iso-Butyl Malonic.	——	65.0
Di-Methyl Malonic.	270 Min.	22.2
Di-Ethyl Malonic.	——	17.6

Sudborough and Feilman[*] carried out a series of investigations on the hydrolysis of the esters of dibasic acids and announced in conclusion that there were two factors which determined the rate of the reaction: the configuration of the acid molecule, and the strength of the acid as determined by its affinity constant. The first factor is the more prominent, and except for very strong acids obscures the influence of the second. James Walker[*], as already indicated, seems to favor the view that for acids such as those of the oxalic series, the first factor determines the second; that is, the configuration of the acid, and not so much the individual nature of the intervening group, detemines the strength of the acid.

Another series of investigations was recently carried on by Fischer and Dilthey[*], who measured the rate of the reaction which takes place when ammonia is allowed to act on alkyl malonic and other esters. The results obtained furnished additional data on the question of steric hindrance. With liquid ammonia at 17 C, they obtained the following results:—

Amide Formed.	Time.	% of Ester Changed.
Malonamide.	10 days	63
Methyl Malonamide.	28 days	50

Amide Formed.	Time.	% Ester Changed.
Ethyl Malonamide.	21 days	63
Propyl Malonamide.	21 days	89
Di-Ethyl Malonamide.	60 days	1.1
Di-Propyl Malonamide.	60 days	2.6

Numbers similar to these were obtained at temperatures up to 150°C with alcoholic ammonia saturated at 0°C.

These data show how very much more easily chemical reagents attack the carboxyl groups when only simple groups are present in the molecule ,than when the groups are more complex.It is difficult to conceive how differences so great as these should be caused by the mere difference in nature of the substituting group,unless some condition of the nature of steric interference existed in the molecule.

A few other determinations made on the physical properties of malonic acids should be mentioned here.

Einhorn*recently observed that di-ethyl malonic acid in various ways shows abnormal reactions.For example it polymerizes in benzene.

Determinations of the solubilities of mono-substituted malonic acids show that they are all very soluble in water except the di-alkyl derivatives,and that the introduction of a second alkyl group invariably diminishes the solubility.Those with an odd number of carbon atoms are more soluble than those with an even number. A similar statement might be made regarding the melting points; Solonina*found that the acids with an uneven number of carbon atoms in the molecule have the higher melting points.

As the malonic acids so far studied have been,with few exceptions,mono-alkyl substituted derivatives,and as the list of exceptions include only two of those which show abnormal reactions, it was thought that it would be of interest to extend the investigation to other more complex acids of the malonic series,and to examine so far as possible the effects of the substituted groups on their electrical conductivity and allied properties.With this object in view measurements were made,the results of which are included and discussed in the following pages.

Preparation of the Malonic Acids.

Most of the malonic acids used were prepared from the corresponding alkyl substitution products of malonic di-ethyl ester by one of the following methods:*—

A.(1), The ester was saponified by means of a strong solution of potassium hydrate, the mixture of the two being heated on a water bath under a reflux condenser until the demarcation between the two liquids had disappeared. In some cases it was found necessary to add alcohol in order to facilitate mixing and thus hasten the reaction.

(2), After as much of the alcohol formed in the reaction had been distilled off as was possible, the volume of the alkyl potassium malonate solution was doubled by the addition of distilled water, and an amount of hydrochloric acid, in excess of that required to neutralize the total amount of potassium hydrate used, was added in order to liberate the alkyl substituted malonic acid.

(3), The solution of the acid was then well shaken up with ether, and after separation, the ethereal solution evaporated on a water bath. The acid was then allowed to crystallize.

B. For those acids of greater complexity, in the case of which decomposition into compounds of lower molecular weight might be expected to occur, (valeric acid was found sometimes), and in order to eliminate the danger of having present any unchanged ester, another method was frequently used:--

(1),The ester was first saponified as already indicated,and the alcohol distilled off.

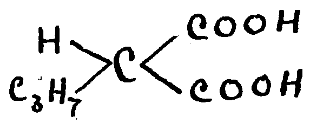
(2),Hydrochloric acid was then added until the solution was just acid towards litmus,under which conditions the alkyl malonic acid was present as the acid potassium salt.An excess of strong calcium chloride solution was then added which precipitated the acid as calcium alkyl malonate.

(3),The precipitate was filtered off,dried and acidified with dilute hydrochloric acid.The free alkyl malonic acid was then extracted with ether and otherwise treated as for the method first described.

This method of preparation gave in most cases a much purer sample of acid than the first method,but the yield was sometimes small,due to the fact that complete precipitation depended on the presence of all the acid as the acid potassium salt.

The method first described shall be referred to as "method A", and the second method as "method B".

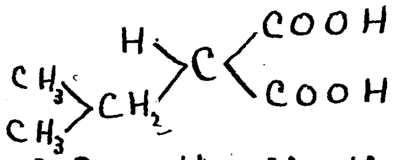
1. Normal Propyl Malonic Acid.



$$\begin{matrix}H\\C_3H_7\end{matrix}\!>C<\!\begin{matrix}COOH\\COOH\end{matrix}$$

This acid was prepared from the normal propyl malonic di-ethyl ester by method A.It had a strong odour of valeric acid, and to purify it was recrystallized from benzene.It was then found to have a melting point of about 94.5°C.After a second recrystallization from benzene it was found to melt sharply at 95.1° C.

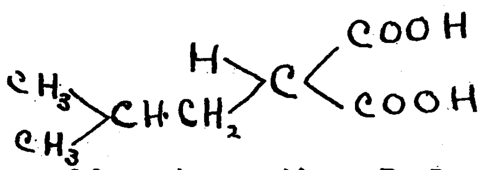
2. Iso-Propyl Malonic Acid.



$$\begin{matrix}H\\ \begin{matrix}CH_3\\CH_3\end{matrix}\!>CH_2\end{matrix}\!>C<\!\begin{matrix}COOH\\COOH\end{matrix}$$

This acid was prepared from the di-ethyl ester corresponding to it by method A.A very good yield was obtained,accompanied by a fair degree of purity. After one recrystallization from benzene the acid had a sharp melting point of 88.6°C.

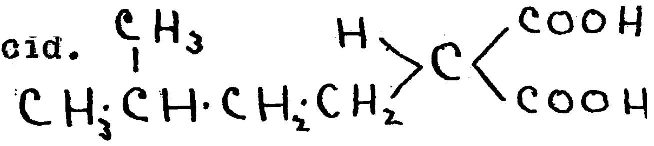
3. Iso-Butyl Malonic Acid.



$$\begin{matrix}H\\ \begin{matrix}CH_3\\CH_3\end{matrix}\!>CH\cdot CH_2\end{matrix}\!>C<\!\begin{matrix}COOH\\COOH\end{matrix}$$

This was prepared according to method B,from Iso-Butyl Malonic ester.The acid crystallized in long-shaped,radiating crystals,which melted sharply at 104.7°C. It seemed very pure and was not further treated.

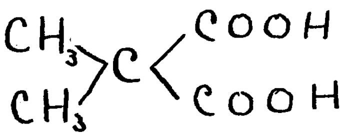
4. Iso-Amyl Malonic Acid.



$$\begin{matrix}H\\ CH_3\overset{\overset{CH_3}{|}}{C}H\cdot CH_2CH_2\end{matrix}\!>C<\!\begin{matrix}COOH\\COOH\end{matrix}$$

This acid was prepared from the ester corresponding to it in the same way as the iso-butyl though it showed different behaviour in two respects: saponification took place very slowly, even when alcohol had been added to bring about the mixing of the two solutions, and on acidifying the calcium salt the solution of the acid floated on the surface of the calcium chloride solution as an oily layer. A good yield of almost pure acid was obtained which, when recrystallized once from benzene, melted sharply at 95.4°C.

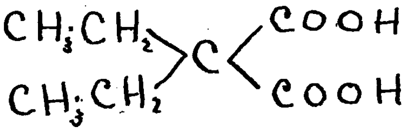
5. Di-Methyl Malonic Acid.



$$\begin{matrix}CH_3\\CH_3\end{matrix}>C<\begin{matrix}COOH\\COOH\end{matrix}$$

The acid employed was obtained from Kahlbaum, but as its melting point was not quite sharp it was recrystallized once from benzene. It then melted sharply at 190.8°C.

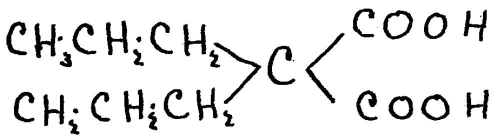
6. Di-Ethyl Malonic Acid.



$$\begin{matrix}CH_3CH_2\\CH_3CH_2\end{matrix}>C<\begin{matrix}COOH\\COOH\end{matrix}$$

Kahlbaum's preparation was employed without further purification as it melted sharply at 125.8°C.

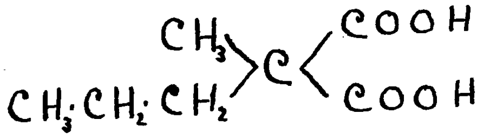
7. Di-Propyl Malonic Acid.



$$\begin{matrix}CH_3CH_2CH_2\\CH_3CH_2CH_2\end{matrix}>C<\begin{matrix}COOH\\COOH\end{matrix}$$

This acid was obtained pure from Kahlbaum, its melting point being very sharp at 157.8°C.

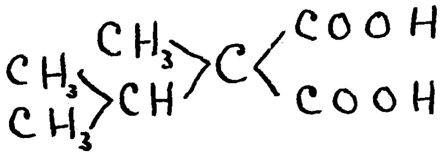
8. Methyl N-Propyl Malonic Acid.



$$\begin{matrix}CH_3\\ CH_3\cdot CH_2\cdot CH_2\end{matrix}\!\!>C<\!\!\begin{matrix}COOH\\ COOH\end{matrix}$$

Dr Walker prepared and purified this acid.It melted sharply at 101.4°C.

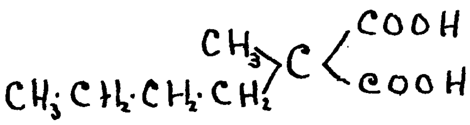
9. Methyl Iso-Propyl Malonic Acid.



$$\begin{matrix}CH_3\\ \begin{matrix}CH_3\\ CH_3\end{matrix}\!\!>CH\end{matrix}\!\!>C<\!\!\begin{matrix}COOH\\ COOH\end{matrix}$$

This acid was also prepared by Dr Walker,but was still in a rather impure state.It was recrystallized from benzene and found to have a melting point of 123.9°C.

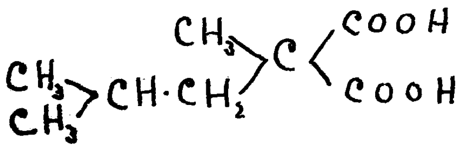
10. Methyl N-Butyl Malonic Acid.



$$\begin{matrix}CH_3\\ CH_3\cdot CH_2\cdot CH_2\cdot CH_2\end{matrix}\!\!>C<\!\!\begin{matrix}COOH\\ COOH\end{matrix}$$

The ester corresponding to this acid was treated in accordance with the method B.After extracting with ether and evaporating,the acid partially solidified as a wet,sticky mass. It was dried and recrystallized from benzene.Its melting point was rather indefinite and was about 81.6——82.5°.It was again recrystallized and now melted sharply at 82.3°C.

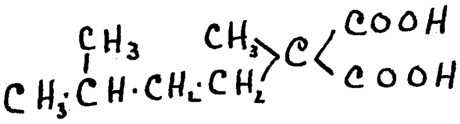
11. Methyl Iso-Butyl Malonic Acid.



$$\begin{matrix}CH_3\\ \begin{matrix}CH_3\\ CH_3\end{matrix}\!\!>CH\cdot CH_2\end{matrix}\!\!>C<\!\!\begin{matrix}COOH\\ COOH\end{matrix}$$

This acid was prepared from the ester corresponding to it and proved to be one of the most difficult to obtain in a crystalline form.This difficulty was afterwards found to be due to the saponification being only partial.The partially saponified ester was heated again on a water-bath with potassium hydrate solution and alcohol for several hours. The saponification then seemed complete and the acid was precipitated in the form of the calcium salt and extracted in the usual way. The acid had a melting point of 118.4°C, and as there was every indication of purity and as the amount of the acid obtained was very small, it was used without further treatment.

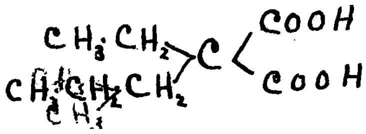
12. Methyl Iso-Amyl Malonic Acid.



$$\begin{matrix} CH_3 & & CH_3 \\ | & & \\ CH_3 \cdot CH \cdot CH_2 \cdot CH_2 & \end{matrix} > C < \begin{matrix} COOH \\ COOH \end{matrix}$$

The acid used was prepared from the methyl iso-amyl malonic ester by method B. A good yield of fairly pure acid was obtained which had a melting point of129—130°C. It was recrystallized once from benzene, then melting at 130.9°C, quite sharply.

13. Ethyl N-Propyl Malonic Acid.



$$\begin{matrix} CH_3 \cdot CH_2 \\ CH_3 \cdot CH_2 \cdot CH_2 \end{matrix} > C < \begin{matrix} COOH \\ COOH \end{matrix}$$

The acid was prepared by Dr Walker and was received from him in three fractions:—

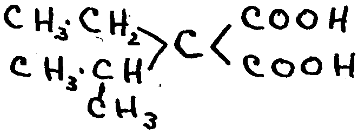
(1), M.P.—114°C.

(2), M.P.—111°C.

(3), M.P.—103°C.

Fraction (1) was again fractionally crystallized from benzene, the first crop of crystals which separated out being retained for use in the experimental work. A melting point of 114.3°C was observed for them.The acid separated from benzene in a well-defined crystalline form,but on standing changed into a white powder,due probably to the loss of benzene of crystallization.

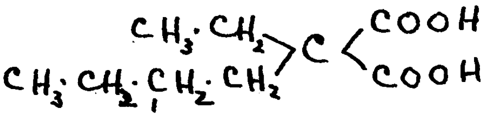
14. Ethyl Iso-Propyl Malonic Acid.



$$\begin{matrix}CH_3\cdot CH_2\\ CH_3\cdot \underset{CH_3}{CH}\end{matrix}>C<\begin{matrix}COOH\\ COOH\end{matrix}$$

The ester from which this acid was prepared was received in two fractions, one boiling at 233 — 236°C,and the other at 228 — 233°C. The two were mixed and saponified together, about 30 hours' boiling being necessary for complete saponification. A very small yield of acid which melted sharply at 72.3°C was obtained ,and owing to the smallness of the amount,it was not further purified.

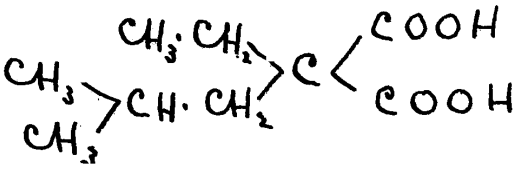
15.Ethyl N-Butyl Malonic Acid.



$$\begin{matrix}CH_3\cdot CH_2\\ CH_3\cdot CH_2\cdot CH_2\cdot CH_2\end{matrix}>C<\begin{matrix}COOH\\ COOH\end{matrix}$$

The preparation of this acid from the ester showed no anomalies not already mentioned in reference to some of the preceding acids.Saponification took place comparatively easily. The acid melted sharply at 115.8°C,so that it was not considered necessary to recrystallize it.Method B was used in its preparation.

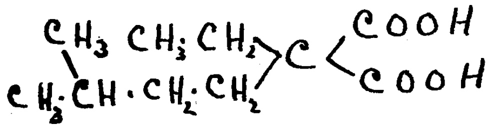
16. Ethyl Iso-Butyl Malonic Acid.



$$\begin{matrix}CH_3\cdot CH_2\\ \begin{matrix}CH_3\\ CH_3\end{matrix}>CH\cdot CH_2\end{matrix}>C<\begin{matrix}COOH\\ COOH\end{matrix}$$

The ethyl iso-butyl malonic acid was prepared from the ester corresponding to it. It was precipitated as the calcium salt with which some of the acid also came down. After recrystallizing once from benzene it melted sharply at 108.8°C. The ester of this acid was extremely difficult to saponify, and for this reason the yield was small.

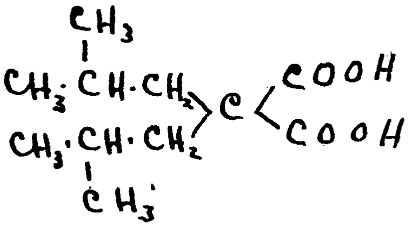
17. Ethyl Iso-Amyl Malonic Acid.



$$\begin{matrix} CH_3\quad CH_3{\cdot}CH_2 \\ CH_3{\cdot}CH{\cdot}CH_2{\cdot}CH_2 \end{matrix}\!>C<\!\begin{matrix} COOH \\ COOH \end{matrix}$$

It was prepared from the ester. The saponification was fairly rapid, and when acidified the acid floated as an oil on the surface of the potassium chloride solution. The acid was recrystallized once from benzene and had then a melting point of 115.0°C.

18. Di-Iso-Butyl Malonic Acid.



$$\begin{matrix} CH_3 \\ | \\ CH_3{\cdot}CH{\cdot}CH_2 \\ CH_3{\cdot}CH{\cdot}CH_2 \\ | \\ CH_3 \end{matrix}\!>C<\!\begin{matrix} COOH \\ COOH \end{matrix}$$

This acid was prepared from the di-iso-butyl malonic ester (B.P. greater than 245°C), which was of doubtful purity. After precipitation as the calcium salt and extraction in the usual way a small amount of acid was obtained which had a sharp melting point of ~~102.~~ 96.0°C. It was recrystallized once from benzene but its melting point did not change.

Conclusions.

Observations made during the preparations of these acids brought the following facts to light:--

(1).That the preparation of the acid by the precipitation of its calcium salt yields a purer acid than would be obtained by complete liberation and direct extraction with ether.

(2).That the rate at which saponification takes place depends on the nature and the complexity of the substituting alkyl groups. Mono-alkyl derivatives are easily saponified and become less so as the number of carbon atoms in the molecule increases.Of the di-alkyl derivatives the iso-alkyl compounds are more difficult to saponify than the normal alkyl compounds,the iso-alkyl compounds arrangeing themselves in the following order: iso-propyl,iso-amyl, iso-butyl.

Hydrolysis of the Normal Barium and Potassium Salts in Dilute Solution.

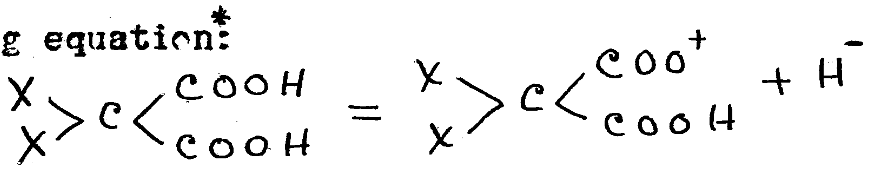
In order to ascertain whether or not the malonic acids, the preparation of which have been described, corresponded to the formulae assigned to them, carefully weighed samples of each were dissolved in water and titrated against potassium hydrate solution which had been standardized by means of N/10 oxalic acid solution. From the volume of alkali solution used, the weight of the acid which would contain two grams of replaceable hydrogen was calculated. This weight would correspond to the molecular weight, provided the substance was what it was thought to be.

The first acids tested in this way, n-propyl, iso-propyl and iso-butyl malonic acids, yielded satisfactory results. When those of higher molecular weight containing the more complex alkyl radicals were tested abnormal values were obtained which were in every case higher than the theoretical values as calculated from the formulae. Another peculiarity was observed. The end point of the titration, as indicated by phenolphthalien, was not sharp as in the case of the simpler acids; a faint shade of pink appeared which grew darker very slowly as more alkali was added.

It was extremely improbable that this behaviour was due to accidental impurities,and in order to further test it,dilute baryta solution was used instead of the dilute potassium hydrate solution.The results were similar to those first obtained. A strong solution of baryta was next used and the acids which gave abnormal values were again titrated.The values now obtained agreed very closely with the theoretical values,and this was especially so when the precipitate of the calcium salt appeared during the titration,a circumstance that was usual with concentrated baryta solution and exceptional with the dilute baryta solution.This exceptional behaviour with dilute alkali solution occurred in two cases and the results obtained indicate the probable explanation.

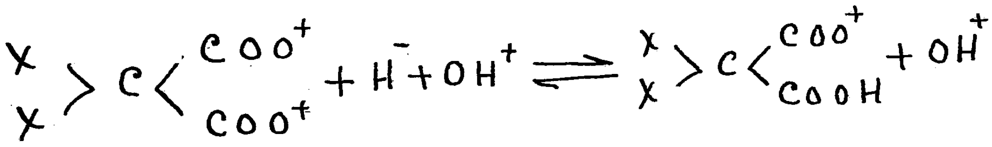
Di-propyl malonic acid,with a calculated molecular weight of 188,gave with dilute potassium hydrate solution a value of 217.7.With concentrated baryta solution it gave a value of 188.5. When dilute baryta solution was used a value of 224 was first obtained,but on standing for a few minutes a precipitate of the barium salt separated out and at the same time the colour due to the indicator disappeared.A volume of dilute baryta solution sufficient to restore the colour was added,and the value then found was188.5. The solution after this remained permanently pink.

In solution a dibasic acid is thought to break up according to the following equation*:



$$\substack{X\\X}{>}C{<}\substack{COOH\\COOH} = \substack{X\\X}{>}C{<}\substack{COO^+\\COOH} + H^-$$

Since in the case of a dibasic organic acid such as this the ion $\substack{X\\X}{>}C{<}\substack{COO^+\\COOH}$ is more stable than the ion $\substack{X\\X}{>}C{<}\substack{COO^+\\COO^+}$ there is a tendency for the former to be produced at the expense of the latter, an equilibrium being set up between it and the partially dissociated water:—



$$\substack{X\\X}{>}C{<}\substack{COO^+\\COO^+} + H^- + OH^+ \rightleftharpoons \substack{X\\X}{>}C{<}\substack{COO^+\\COOH} + OH^+$$

An amount of hydrogen ions is thus present which is not sufficient to neutralize the amount of hydroxyl ions present, the solution thus giving an alkaline reaction.

This is probably what happens in the titrations with dilute alkali solution In the case of these acids the barium salts of which separate easily in the solid state, the amount of the salt in solution would be very small and the amount of free neutral anions $\substack{X\\X}{>}C{<}\substack{COO^+\\COOH}$ correspondingly small.

The question of hydrolysis of these salts will be further discussed later.

The results obtained are tabulated on the following page.

Table 1.

Hydrolysis of the Barium and Potassium Salts of the Malonic Acids.

Acid.	Mol.Wt. Calculated.	Mol.Wt.by KOH .1N	Mol.Wt.by Ba(OH) .03N.	Mol.Wt.by Ba(OH) .26N.
N-Propyl Malonic.	146	146.5	——	——
I-Propyl Malonic.	146	146.4	——	——
I-Butyl Malonic.	160	160.7	——	——
I-Amyl Malonic.	174	177.7	228	174.1
Di-Methyl Malonic.	132	132.3	——	——
Di-Ethyl Malonic.	160	168.1	169	159.8
Di-Propyl Malonic.	188	217.7	223.8	188.5
Di-I-Butyl Malonic.	216	——	——	215.1
Methyl N-Propyl Malonic.	160	157.7	160.6	158.6
Methyl I-Propyl Malonic.	160	160.2	——	——
Methyl N-Butyl Malonic.	174	——	201.4	174.6
Methyl I-Butyl Malonic.	174	——	191.2	173.4
Methyl I-Amyl Malonic.	188	195.5	213.3	188.7
Ethyl N-Propyl Malonic.	174	——	184.7	173.6
Ethyl I-Propyl Malonic.	174	——	——	174.4
Ethyl N-Butyl Malonic.	188	221.8	——	188.6
Ethyl I-Butyl Malonic.	188	——	247.3	188.4
Ethyl I-Amyl Malonic.	202	226.2	222.8	201.7

Table 2.

Acids Showing Exceptional Behaviour on Titration with Dilute Alkali.

Acid.	Mol.Wt. Calculated.	Mol.Wt.by Ba(OH) .03N	Same,After Standing.
Di-Propyl Malonic.	188	223.8	188.5
Ethyl I-Amyl Malonic.	202	222.8	203.4

Another point was observed in the titrations of the acids which should be mentioned ,though it was not further investigated. Owing to the fact that some of the acids of higher molecular weight were very difficultly soluble in water,a small amount of alcohol was added to facilitate the process.It was assumed at the time that the presence of the alcohol would not appreciably affect the titration.This assumption however,was found to be erroneous except possibly in the case of those acids not hydrolized in purely aqueous solution,as will be seen from the following results:—

Table 3.

Acid.	Mol.Wt. Calculated.	Mol.Wt.in C_2H_5OH,(pure)	Mol.Wt.in Water and Alcohol.
Ethyl I-Amyl Malonic.	202	277.3	250.8
Ethyl N-Butyl Malonic.	188	----	233.4
Methyl N-Propyl Malonic.	160	----	162.1

The decided rise in the values found by titration due to the addition of alcohol, as indicated above, is probably caused by the formation of some malonic ester in the molecular condition, or of some malonic mono-ethyl ester (or acid ester), in the ionic condition. By analogy we should expect the latter. Either of these reactions would cause an increase in the number of hydroxyl ions present and so decrease the amount of alkali necessary to obtain an end point.

Melting Points of the Malonic Acids.

The melting points of the alkyl substituted malonic acids were determined by putting some of the finely ground acid into a capillary tube, fastened to the side of a thermometer, and heating slowly in a double bath of strong sulphuric acid. The acid in the inside vessel, in which the capillary tube was immersed was kept well stirred by a glass stirrer. The melting point of the acid was taken to be that temperature at which the sample in the fine tube became transparent.

Very few regularities are apparent in the results obtained in these melting point determinations, except perhaps in these which contain iso- groups. In the case of the mono-substituted derivatives the results are peculiar, the melting point rising and then falling again as the molecular weight is increased. Iso-propyl malonic acid melts at 89°C. Iso-amyl malonic acid melts at 95°C. The intervening derivative, iso-butyl malonic acid has a much higher melting point,105°C.It is difficult to understand why this should be so,but it must be due to some internal condition in the molecule and probably not to any peculiarity of the iso-butyl group.In the methyl iso-alkyl malonic acids,the melting points rise with increasing complexity,but not regularly. In the following table the melting points obtained are arranged, and for the sake of comparison,those given by Band* and those determined by Walden* in connection with his electrical conductivity measurements.

Table 4.

Melting Points of the Malonic Acids.

Acid.	M.P.Prev. Found	M.P.BY Walden.	M.P. Found.
N-Propyl Malonic.	96°C.	94—96°	95.1°
Iso-Propyl Malonic.	87°	87—90°	88.6°
Iso-Butyl Malonic.	107°	107°	104.5°
Iso-Amyl Malonic.	93°	——	95.4°
Di-Methyl Malonic.	185—186°	——	190.8°
Di-Ethyl Malonic.	125°	120—121°	125.8°
Di-Propyl Malonic.	158°	——	157.8°
Di-Iso-Butyl Malonic.	——	——	96.9°
Methyl N-Propyl Malonic.	106°	——	101.4°

Table 4.

Acid	M.P.Prev. Found.	M.P.By Walden.	M.P. Found.
Methyl Iso-Propyl Malonic.	124°	----	125.1°
Methyl N-Butyl Malonic.	----	----	82.3°
Methyl Iso-Butyl Malonic.	----	----	118.4°
Methyl Iso-Amyl Malonic.	----	----	130.9°
Ethyl N-Propyl Malonic.	----	----	114.3°
Ethyl Iso-Proptl Malonic.	----	----	72.3°
Ethyl N-Butyl Malonic.	----	----	115.8°
Ethyl Iso-Butyl Malonic.	----	----	102.8°
Ethyl Iso-Amyl Malonic.	----	----	115.0°

Electrical Conductitities of the Acids in Aqueous Solution.

Carefully weighed quantities of the purified acids were dissolved in water and made up to the volume required for a 1/16 molar, or in the case of the less soluble acids for a 1/32 molar solution. The method of measurement was similar to that described by Ostwald,* the resistance of the solution being determined by means of a standard resistance box, a Wheatstone's bridge and a telephone receiver. The temperature of the thermostat was regulated automatically by the usual electrical method, and was kept at 25°C, constant to about .07 of one degree.*

The water used was specially distilled from a solution of potassium hydrate made with the ordinary distilled water of the laboratory.* The conductivity as measured for the various stages of its purification was as follows:--

(1), Ordinary distilled water.	---	Spec.Cond.	3.1×10^{-4}	l.
(2), Sample (1), redistilled.	---	Spec.Cond.	3.63×10^{-5}.	?
(3), Sample (2), redistilled.	---	Spec.Cond.	2.62×10^{-5}.	?
(4), Sample (1), redistilled from KOH.-		Spec.Cond	2.34×10^{-6}.	

The correction for the conductivity of the water amounted to about 2.35 units at a dilution of 1024 litres. This correction was applied to the molecular conductivities. The water was distilled through a block-tin condenser and was afterwards retained in a tightly stoppered Jena glass flask.

The bridge wire was of platinum and was carefully calibrated. The resistance capacity of the conductivity cell was found by using a 1/50 normal solution of pure, fused potassium chloride; the value found being .1007.

In the following tables the letters employed have the significations noted below:--

V=the dilution in c.cm.

M_v=the molecular conductivity at dilution V.

M_∞=the molecular conductivity at infinite dilution.

m=the degree of dissociation.

k=the dissociation constant.

c=the conductivity in reciprocal ohms.

s=the specific conductivity in reciprocal ohms.

Table 5.

Normal Propyl Malonic Acid. M_∞=369.

$V\times10^{-3}$	$C\times10^{4}$	$S\times10^{5}$	m	M	$K\times10^{5}$
16	293	294.6	.128	47.10	0.116
32	194.5	195.9	.170	62.62	0.111
64	129.4	130.31	.225	83.25	0.102
128	85.7	86.3	.300	110.46	0.113
256	54.4	55.27	.404	149.00	0.107
512	34.46	34.79	.470	173.47	0.094
1024	21.56	21.76	.599	220.50	0.089

Most probable value of $K\times10^{5}$ is 0.111

Iso-Propyl Malonic Acid. M_∞=368

$V\times10^{-3}$	$C\times10^{4}$	$S\times10^{5}$	m	M	$K\times10^{5}$
16	306.9	308.90	.134	49.38	0.129
32	213.7	215.40	.186	68.85	0.132
64	141.92	143.00	.248	91.37	0.128
128	93.53	94.20	.335	120.28	0.131
256	60.12	60.56	.415	153.15	0.115
512	36.82	37.08	.521	188.69	0.111
1024	21.61	21.76	.599	220.49	0.0874

Most Probable value of $K\times10^{5}$ is 0.130

Iso-Butyl Malonic Acid. $M_\infty = 366$

$V \times 10^{-3}$	$C \times 10^{4}$	$S \times 10^{5}$	m	M	$K \times 10^{5}$
16	264.27	266.15	.116	42.55	0.095
32	183.91	186.61	.162	59.64	0.097
64	129.64	130.59	.227	83.43	0.104
128	87.33	87.95	.307	112 28	0.106
256	57.80	58.02	.403	147.93	0.106
512	37.22	37.37	.534	189.54	0.119
1024	22.87	23.03	.637	233.52	0.109

Most probable value of $K \times 10^{5}$ is 0.096

Iso-Amyl Malonic Acid. $M_\infty = 367$

$V \times 10^{-3}$	$C \times 10^{4}$	$S \times 10^{5}$	m	M	$K \times 10^{5}$
16	303.15	305.31	.133	48.81	0.114
32	209.81	211.79	.184	67.70	0.129
64	143.07	144.21	.249	91.42	0.129
128	96.34	97.02	.337	123.90	0.133
256	62.81	63.28	.440	161.40	0.135
512	39.98	40.27	.560	205.01	0.139
1024	24.35	24.53	.678	248.15	0.140

Most probable value of $K \times 10^{5}$ is 0.126

Di-Methyl Malonic Acid. $M_{\infty}=369$.

$V\times10^{-3}$	$C\times10^{4}$	$S\times10^{5}$	m	M	$K\times10^{5}$
16	238.9	240.59	.104	38.86	0.075
32	170.27	171.48	.148	54.80	0.080
64	116.19	117.02	.202	74.74	0.079
128	78.05	78.45	.271	100.13	0.078
256	51.34	51.70	.361	131.77	0.079
512	32.97	33.21	.458	169.43	0.076
1024	20.44	20.60	.565	208.54	0.072

Most probable value of $K\times10^{5}$ is 0.077

Di-Ethyl Malonic Acid. $M_{\infty}=361$.

$V\times10^{-3}$	$C\times10^{4}$	$S\times10^{5}$	m	M	$K\times10^{5}$
16	626.7	629.1	.288	105.10	0.750
32	421.3	423.4	.382	138.09	0.751
64	274.12	275.9	.495	179.56	0.775
128	165.7	167.3	.614	222.31	0.783
256	90.9	91.2	.730	264.43	0.799
512	55.1	56.7	.827	298.00	0.752

Most probable value of $K\times10^{5}$ is 0.751

Di-Propyl Malonic Acid. $M_\alpha=360$.

$V \times 10^{-3}$	$C \times 10^{4}$	$S \times 10^{5}$	m	M	$K \times 10^{5}$
32	509.4	512.83	.461	164.03	1.191
64	319.76	322.01	.571	205.95	1.196
128	193.44	194.73	.690	248.76	1.197
256	111.39	112.18	.796	286.59	1.073
512	64.55	65.01	.920	331.66	2.135
1024	34.41	34.65	.978	352.50	4.798

Most probable value of $K \times 10^{5}$ is 1.194

Di-Iso-Butyl Malonic Acid. $M_\alpha=372$.

$V \times 10^{-3}$	$C \times 10^{4}$	$S \times 10^{5}$	m	M	$K \times 10^{5}$
32	221.20	222.77	.192	71.21	0.141
64	100.08	101.40	.261	96.88	0.143
128	67.41	67.89	.348	129.49	0.144
256	43.74	44.05	.465	173.22	0.158
512	27.44	27.65	.601	224.37	0.178
1024	16.86	16.98	.755	280.77	0.228

Most probable value of $K \times 10^{5}$ is 0.142

Mthyl Normal Propyl Malonic Acid. $M_\infty = 357$.

$V \times 10^{-3}$	$C \times 10^{4}$	$S \times 10^{5}$	m	M	$K \times 10^{5}$
16	368.77	371.38	.166	59.38	0.207
32	254.86	256.68	.229	82.06	0.214
64	170.53	171.71	.307	109.75	0.214
128	112.43	113.44	.405	144.91	0.217
256	71.86	72.39	.516	184.70	0.218
512	45.25	45.58	.649	232.17	0.235
1024	26.92	27.11	.771	275.26	0.252

Most probable value of $K \times 10^{5}$ is 0.212

Methyl Iso-Propyl Malonic Acid. $M_\infty = 358$.

$V \times 10^{-3}$	$C \times 10^{4}$	$S \times 10^{5}$	m	M	$K \times 10^{5}$
32	213.73	215.25	.192	68.81	0.144
64	145.44	146.47	.256	93.59	0.146
128	97.36	98.04	.349	125.20	0.146
256	63.42	63.49	.441	158.13	0.137
512	39.98	40.25	.571	204.91	0.149
1024	24.25	24.43	.690	247.76	0.150

Most probable value of $K \times 10^{5}$ is 0.145

Methyl Normal Butyl Malonic Acid. $M_\infty = 349$.

$V \times 10^{-3}$	$C \times 10^{4}$	$S \times 10^{5}$	m	M	$K \times 10^{5}$
32	230.13	231.76	.213	74.09	0.178
64	154.20	155.30	.284	99.25	0.176
128	100.93	101.64	.381	129.81	0.173
256	64.84	65.30	.477	166.58	0.172
512	39.68	39.96	.581	203.44	0.158
1024	23.31	23.48	.680	238.06	0.142

Most probable value of $K \times 10^{5}$ is 0.175.

Methyl Iso-Butyl Malonic Acid. $M_\infty = 352$.

$V \times 10^{-3}$	$C \times 10^{4}$	$S \times 10^{5}$	m	M	$K \times 10^{5}$
32	315.84	318.08	.276	101.71	0.369
64	211.12	212.66	.386	135.94	0.380
128	137.40	138.38	.501	176.83	0.397
256	86.44	86.40	.627	220.60	0.407
512	52.04	52.44	.758	267.31	0.465
1024	30.00	30.21	.871	307.03	0.581

Most probable value of $K \times 10^{5}$ is 0.369.

Methyl Iso-Amyl Malonic Axid. $M_\infty = 355$.

$V \times 10^{-3}$	$C \times 10^{4}$	$S \times 10^{5}$	m	M	$K \times 10^{5}$
32	256.04	257.86	.231	82.44	0.217
64	171.30	172.52	.311	110.27	0.218
128	112.47	113.17	.407	144.56	0.220
256	72.48	73.00	.512	182.28	0.211
512	45.03	45.35	.651	230.99	0.236
1024	26.66	26.85	.766	272.56	0.250

Most probable value of $K \times 10^{5}$ is 0.218

Ehtyl Normal Propyl Malonic Acid. $M_\infty = 365$.(?)

$V \times 10^{-3}$	$C \times 10^{4}$	$S \times 10^{5}$	m	M	$K \times 10^{5}$
16	766.60	772.04	.337	123.49	1.071
32	506.00	509.59	.419	163.00	1.125
64	317.85	320.10	.560	204.72	1.124
128	193.91	195.28	.684	249.67	1.163
256	112.19	112.98	.791	288.64	1.176
512	62.54	62.98	.880	321.29	1.253
1024	33.56	33.80	.941	343.76	1.508

Most probable value of $K \times 10^{5}$ is 1.106.

Ethyl Iso-Propyl Malonic Acid. $M_{\infty} = 364$.

$V \times 10^{-3}$	$C \times 10^{4}$	$S \times 10^{5}$	m	M	$K \times 10^{5}$
32	286.40	288.43	.254	92.22	0.267
64	186.38	187.71	.329	119.99	0.254
128	120.34	121.19	.425	154.83	0.248
256	75.73	76.26	.533	194.65	0.244
512	47.05	47.38	.661	241.41	0.257
1024	28.16	28.47	.784	288.55	0.298

Most probable value of $K \times 10^{5}$ is 0.254.

Ethyl Normal Butyl Malonic Acid. $M_{\infty} = 356$.

$V \times 10^{-3}$	$C \times 10^{4}$	$S \times 10^{5}$	m	M	$K \times 10^{5}$
32	500.11	503.69	.454	161.11	1.166
64	319.26	321 55	.567	205.65	1.242
128	195.45	196.84	.683	251.66	1.338
256	114.35	115.16	.810	294.22	1.527
512	64.35	64.81	.912	330.64	2.299
1024	34.72	34.97	.980	355.74	——

Probable value of $K \times 10^{5}$ is1.166

Ethyl Iso-Butyl Malonic Acid. $M_\alpha = 354$.

$V\times10^{-3}$	$C\times10^{4}$	$S\times10^{5}$	m	M	$K\times10^{5}$
32	595.7	596.34	.537	190.76	1.975
64	354.38	356.90	.643	228.27	1.821
128	213.80	216.32	.780	276.59	1.946
256	113.12	113.92	.821	291.04	1.869
512	61.81	62.25	.862	316.55	——
1024	33.44	33.69	.963	342.59	2.347

Probable value of $K\times10^{5}$ is 1.904.

Ethyl Iso-Amyl Malonic Acid. $M_\alpha = 355$.

$V\times10^{-3}$	$C\times10^{4}$	$S\times10^{5}$	m	M	$K\times10^{5}$
32	475.32	478.70	.430	153.11	1.020
64	303.30	307.38	.552	196.58	1.064
128	184.81	186.12	.670	237.94	1.065
256	107.42	108.18	.779	276.35	1.061
512	60.94	61.12	.873	310.82	1.209
1024	32.77	33.01	.939	334.62	1.547

Probable value of $K\times10^{5}$ is 1.053.

Electrical Conductivities of the Normal Sodium Salts in Aqueous Solution.

In order to obtain the molecular conductivities of the malonic acids at infinite dilution the electrical conductivities of the normal sodium salts were determined, with the erroneous idea that the dibasic anion $\begin{matrix}Y\\X\end{matrix}>C<\begin{matrix}COO^+\\COO^+\end{matrix}$ would convey an equal amount of electricity as the mono-basic anion $\begin{matrix}Y\\X\end{matrix}>C<\begin{matrix}COO^+\\COOH\end{matrix}$ would. It was considered that the difference in mass between the two ions due to one atom of hydrogen would have a negligible influence on the velocity. The fact that the neutral anion would convey a double charge, was at first over-looked.

Although the results obtained were not used for the purpose for which they were originally intended, yet since they throw additional light on the subject of hydrolysis, which has already been discussed, and since they furnish us with data concerning the different velocities, or conductivities, of the acid and the neutral anions respectively, the values obtained are included in the determinations reported.

The solution of the di-sodium salt was prepared by adding 20 c.cm. of N/8 sodium hydrate solution to an equal volume of a solution of the acid, M/16. The solution obtained was then N/16, or M/32. The solutions of higher dilution were obtained by removing half and diluting with conductivity water to the original volume.*

Table 6.

Electrical Conductivities of the Normal Sodium Salts in Aqueous Solution.

Di-Sodium Normal Propyl Malonate. $M_{\infty}=182$.

$V \times 10^{-3}$	$C \times 10^{4}$	$S \times 10^{5}$	M	$K \times 10^{5}$ by Rudolphi's Rule.
32	462.46	465.71	148.99	0.654
64	248.83	250.09	159.98	0.799
128	131.92	133.06	170.02	1.169
256	69.10	69.59	177.55	2.72
512	35.40	35.55	180.26	
1024	17.91	18.03	182.23	

Di-Sodium Iso-Propyl Malonate. $M_{\infty}=190$.

$V \times 10^{-3}$	$C \times 10^{4}$	$S \times 10^{5}$	M	$K \times 10^{5}$
32	464.70	468.49	149.84	0.524
64	249.03	250.80	160.37	0.561
128	131.22	132.13	168.83	0.640
256	68.66	69.12	176.35	0.728
512	35.38	35.78	182.03	
1024	18.29	18.42	185.25	

Di-Sodium Iso-Butyl Malonate. $M_\infty=187$.

$V\times10^{-3}$	$C\times10^{4}$	$S\times10^{5}$	M	$K\times10^{5}$
32	449.58	452.31	144.70	0.474
64	244.24	245.97	155.35	0.502
128	130.96	131.84	168.46	0.702
256	68.47	69.13	176.39	0.941
512	35.16	35.41	180.12	
1024	18.15	18.28	184.79	

Di-Sodium Iso-Amyl Malonate. $M_\infty=180$.

$V\times10^{-3}$	$C\times10^{4}$	$S\times10^{5}$	M	$K\times10^{5}$
32	444.19	447.24	143.08	0.543
64	239.37	240.16	154.21	0.638
128	125.23	126.12	161.24	0.670
256	66.07	66.54	166.74	0.745
512	33.96	34.20	173.93	
1024	17.35	17.47	176.52	

Di-Sodium Di-Methyl Malonate. $M_\infty=192$.

$V\times10^{-3}$	$C\times10^{4}$	$S\times10^{5}$	M	$K\times10^{5}$
32	477.42	481.81	154.11	0.575
64	255.47	257.28	164.36	0.626
128	136.53	137.48	175.68	0.892
256	70.51	71.01	181.20	0.970
512	36.54	36.78	187.12	
1024	18.81	18.94	191.64	

Di-Sodium Di-Ethyl Malonate. $M_\infty=192$.

$V\times10^{-3}$	$C\times10^{4}$	$S\times10^{5}$	M	$K\times10^{5}$
32	498.5	502.04	160.62	0.553
64	272.91	274.84	175.83	0.737
128	143.49	144.47	184.62	0.882
256	74.39	74.92	191.40	1.025
512	38.42	38.69	196.92	

Di-Sodium Di-Propyl Malonate. M_α=183.

$V \times 10^{-3}$	$C \times 10^{4}$	$S \times 10^{5}$	M	$K \times 10^{5}$
64	237.52	239.20	152.94	0.533
128	126.26	127.16	162.46	0.600
256	65.51	65.98	166.71	0.554
512	34.08	34.33	174.59	0.924
1024	17.59	17.72	179.05	

Di-SodiumDi-Iso-Butyl Malonate. M_α=194.

$V \times 10^{-3}$	$C \times 10^{4}$	$S \times 10^{5}$	M	$K \times 10^{5}$
64	223.16	224.74	143.69	0.267
128	122.12	122.98	157.12	0.304
256	64.32	64.78	165.28	0.303
512	34.62	34.71	176.52	0.392
1024	17.99	18.14	185.71	

Di Sodium Methyl Normal Propyl Malonate. $M_\infty = 202$.

$VX10^{-3}$	$CX10^{4}$	$SX10^{5}$	M	$KX10^{5}$
32	467.90	471.19	150.71	0.391
64	252.08	253.87	162.33	0.406
128	133.73	134.67	172.08	0.431
256	70.60	71.10	181.43	0.483
512	37.04	37.31	189.83	0.658
1024	19.29	19.42	196.54	

Di-Sodium Methyl Iso-Propyl Malonate. $M_\infty = 202$.

$VX10^{-3}$	$CX10^{4}$	$SX10^{5}$	M	$KX10^{5}$
64	211.31	212.81	136.05	0.174
128	120.98	122.16	150.62	0.196
256	61.97	62.91	161.54	0.196
512	33.14	33.45	170.97	0.206
1024	17.53	17.80	182.34	

Di-Sodium Methyl Normal Butyl Malonate. $M_\infty = 205$.

$V \times 10^{-3}$	$C \times 10^{4}$	$S \times 10^{5}$	M	$K \times 10^{5}$
64	275.46	277.42	177.40	0.692
128	145.48	146.49	187.21	0.837
256	75.04	75.57	192.88	0.947
512	38.79	39.07	198.84	1.358
1024	20.10	20.24	204.91	
2048				

Di-Sodium Methyl Iso-Butyl Malonate. $M_\infty = 202$.

$V \times 10^{-3}$	$C \times 10^{4}$	$S \times 10^{5}$	M	$K \times 10^{5}$
64	211.58	213.05	136.20	0.173
128	122.54	123.41	157.68	0.239
256	63.60	64.35	164.15	0.222
512	33.82	34.06	173.20	0.262
1024	1776	17.88	180.76	
2048	9.77	9.83	196.66	

Di-Sodium Methyl Iso-Amyl Malonate. $M_\infty = 195$.

$V \times 10^{-3}$	$C \times 10^{4}$	$S \times 10^{5}$	M	$K \times 10^{5}$
64	245.11	246.85	157.84	0.432
128	132.50	133.45	170.52	0.525
256	69.64	70.13	178.95	0.642
512	36.31	36.57	186.04	0.872
1024	18.67	18.82	190.32	
2048	9.71	9.77	195.42	

Di-Sodium Ethyl Normal Propyl Malonate. M_∞ 202.

$V \times 10^{-3}$	$C \times 10^{4}$	$S \times 10^{5}$	M	$K \times 10^{5}$
32	461.29	464.57	148.59	0.367
64	246.70	248.44	158.86	0.362
128	132.20	133.14	170.13	0.395
256	70.43	70.60	180.29	0.456
512	36.98	37.25	189.54	0.658
1024	19.09	19.22	194.50	
2048	10.02	10.09	201.99	

Di-Sodium Ethyl Iso-Propyl Malonate. $M_\infty = 202$.

$V \times 10^{-3}$	$C \times 10^{4}$	$S \times 10^{5}$	M	$K \times 10^{5}$
64	248.70	250.46	160.15	0.377
128	134.29	135.25	172.82	0.451
256	70.48	70.99	181.14	0.483
512	36.71	36.97	188.12	0.553
1024	19.19	19.34	195.64	
2048	10.05	10.12	202.63	

Di-Sodium Ethyl Normal Butyl Malonate. $M_\infty = 200$.

$V \times 10^{-3}$	$C \times 10^{4}$	$S \times 10^{5}$	M	$K \times 10^{5}$
64	234.82	236.48	151.20	0.291
128	125.61	126.50	161.30	0.306
256	66.49	66.97	170.26	0.301
512	35.18	35.43	180.71	0.358
1024	18.33	18.47	186.74	
2048	9.58	9.65	192.90	

Di-Sodium Ethyl Iso-Butyl Malonate. $M_\infty = 200$.

$V \times 10^{-3}$	$C \times 10^{4}$	$S \times 10^{5}$	M	$K \times 10^{5}$
64	252.14	253.93	161.37	0.415
128	132.82	133.77	170.93	0.511
256	70.65	71.13	181.50	0.539
512	37.17	37.44	190.50	0.892
1024	19.34	19.47	197.03	

Di-Sodium Ethyl Iso-Amyl Malonate. $M_\infty = 193$.

$V \times 10^{-3}$	$C \times 10^{4}$	$S \times 10^{5}$	M	$K \times 10^{5}$
64	227.47	229.08	146.47	0.294
128	127.37	128.45	164.12	0.425
256	67.24	67.83	173.06	0.485
512	35.74	36.00	183.12	0.767
1024	18.42	18.56	187.68	
2048	9.52	9.59	191.62	

Electrical Conductivities of the Acid Sodium Salts in Aqueous Solution.

These were determined in order to obtain the conductivity of the mono-basic anion of each of the malonic acids, from which the molecular conductivity of the acid was calculated.

The solution of the acid sodium salt was made up in the same manner as was the solution of the di-sodium salt, 20 c.cm. of N/16 sodium hydrate solution being added to the same volume of the M/16 solution of the acid. The solution of the acid sodium salt of the acid thus obtained had a strength of M/32 or N/16. This solution was then diluted with conductivity water until a solution of 1/128 concentration was obtained. Measurements were then made on the conductivities and the dilution increased as for the measurements already tabulated. In all cases corrections for the conductivity of the water and for irregularities in the bridge-wire were made.

Table 7.

Electrical Conductivities of the Acid Sodium Salts in Aqueous Solution.

Sodium Acid Normal Propyl Malonate. $M_{\infty} = 93$.

$V \times 10^{-3}$	$C \times 10^{5}$	$S \times 10^{6}$	M
128	574.97	579.05	73.82
256	309.01	311.20	79.08
512	165.33	166.58	84.11
1024	87.43	88.05	87.81

Sodium Acid Iso-Propyl Malonate $M_{\infty} = 86$.

$V \times 10^{-3}$	$C \times 10^{5}$	$S \times 10^{6}$	M
128	569.5	573.54	73.12
256	295.00	297.10	75.47
512	155.34	156.49	78.95
1024	82.86	83.45	83.10

Sodium Acid Iso-Butyl Malonate. $M_\infty = 87.5$.

$V \times 10^{-3}$	$C \times 10^{5}$	$S \times 10^{6}$	M
128	575.93	577.97	73.69
256	302.80	303.05	76.99
512	162.16	163.31	82.44
1024	85.33	85.94	85.64

Sodium Acid Iso-Amyl Malonate. $M_\infty = 91.5$.

$V \times 10^{-3}$	$C \times 10^{5}$	$S \times 10^{6}$	M
128	558.67	562.67	72.02
256	300.17	302.30	76.80
512	159.32	160.58	81.04
1024	86.29	87.45	87.19

Sodium Acid Di-Methyl Malonate. $M_\infty = 93$.

$V \times 10^{-3}$	$C \times 10^{5}$	$S \times 10^{6}$	M	$K \times 10^{5}$
32	214.63	216.13	69.13	0.377
64	113.94	114.74	73.36	0.358
128	59.28	59.70	76.42	0.323
256	320.6	32.27	82.07	0.411
512	16.89	17.00	86.94	0.899
1024	9.28	9.34	90.90	

Sodium Acid Di-Ethyl Malonate. M_{∞}= 83.5.

$V\times10^{-3}$	$C\times10^{6}$	$S\times10^{6}$	M
128	583.63	587.78	74.94
256	305.24	307.41	78.11
512	160.76	161.90	81.11
1024	84.14	84.74	82.41 (?)

Sodium Acid Di-Propyl Malonate. M_{∞}= 84.

$V\times10^{-3}$	$C\times10^{6}$	$S\times10^{6}$	M
128	553.57	557.50	71.07
256	283.59	285.60	72.52
512	148.37	149.52	75.38
1024	79.23	79.79	79.35

Sodium Acid Di-Iso-Butyl Malonate. M_{∞}= 96.

$V\times10^{-3}$	$C\times10^{6}$	$S\times10^{6}$	M
128	634.50	639.00	81.50
256	334.21	337.41	86.21
512	177.25	178.49	89.97
1024	91.36	91.99	93.76

Sodium Acid Methyl Normal Propyl Malonate. $M_\infty = 81.$

$VX10^{-3}$	$CX10^{5}$	$SX10^{6}$	M
128	569.57	573.61	73.13
256	298.34	300.46	76.33
512	154.78	155.89	78.64
1024	82.16	82.73	81.40

Sodium Acid Methyl Iso-Propyl Malonate. $M_\infty = 82.5$

$VX10^{-3}$	$CX10^{5}$	$SX10^{6}$	M
128	611.65	616.09	78.57
256	313.29	313.48	79.66
512	160.14	161.28	81.40
1024	83.81	84.39	82.07

Sodium Acid Methyl Normal Butyl Malonate. $M_\infty = 73.50.$

$VX10^{-3}$	$CX10^{5}$	$SX10^{6}$	M
128	570.66	574.71	73.27
256	285.41	287.11	73.21
512	144.10	145.12	73.12
1024	73.38	73.78	73.20

Sodium Methyl Iso-Butyl Malonate. M_α= 76.

$V\times10^{-3}$	$C\times10^{5}$	$S\times10^{6}$	M
128	541.52	543.31	69.76
256	281.62	283.58	72.55
512	143.35	144.36	73.62
1024	74.23	75.61	75.13

Sodium Acid Iso-Amyl Malonate. 79.

$V\times10^{-3}$	$C\times10^{5}$	$S\times10^{6}$	M
128	591.35	595.60	75.94
256	302.43	304.57	77.38
512	153.49	154.92	78.14
1024	78.72	79.31	78.86

Sodium Acid Ethyl Normal Propyl Malonate. 89.5.

$V\times10^{-3}$	$C\times10^{5}$	$S\times10^{6}$	M
128	539.09	543.01	69.22
256	282.60	284.60	72.27
512	147.88	148.92	75.07
1024	78.47	88.63 79.07	88.57 ? (78 61)

Sodium Acid Ethyl Normal Butyl Malonate. $M_\infty = 80.5$.

$V \times 10^{-3}$	$C \times 10^{5}$	$S \times 10^{6}$	M
128	549.43	553.29	69.53
256	290.37	292.40	74.27
512	151.06	152.68	75.00
1024	79.23	79.71	78.27

Sodium Acid Ethyl Iso-Butyl Malonate. $M_\infty = 78$.

$V \times 10^{-3}$	$C \times 10^{6}$	$S \times 10^{6}$	M
128	544.07	547.96	69.84
256	282.77	284.77	72.31
512	145.95	146.98	74.08
1024	77.22	77.86	76.37

Sodium Acid Ethyl Iso-Amyl Malonate. $M_\infty = 74$.

128	535.94	539.74	68.79
256	272.57	274.50	69.68
512	143.32	144.30	72.72
1024	75.32	75.86	73.5

Titration of the acids with dilute alkali show that the normal potassium and barium salts of the alkyl substituted malonic acids are hydrolyzed in dilute aqueous solution, and that the di-alkyl derivatives are hydrolyzed to a greater extent than the mono-alkyl derivatives. Iso-amyl malonate of barium proved to be an exception to this rule.

The results obtained from the conductivity measurements made on the di-sodium salts furnish conclusive proofs that hydrolysis does take place and that mainly in one of the carboxyl groups, since measurements on the mono-sodiumsalts show no indication of any such change taking place. If the values obtained for the molecular conductivities of the normal sodium salts be arranged in the order of increasing dilution, it will be noticed that the molecular conductivity increases continuously and does not approach a constant value. This must be due to new ions being formed in the solution, a greater capacity for electrical conductance being thus obtained. The two most probable ways by which new ions might be formed have already been mentioned: by the formation of the acid anion, thus liberating an increasing amount of hydroxyl, and by the further splitting off of sodium ions, if it be assumed that dibasic dissociation is only partial as in the case of the acids themselves. The first of these hypotheses is the only one which might apply here since the possibility of the second being correct is precluded by the behaviour of the di-propyl and ethyl iso-amyl malonic acids when titrated with dilute baryta solution.

Hydrolysis would have two opposite effects on the conductivity of a solution of a normal alkali salt. The dibasic character of the anion would be destroyed with the resulting formation of a monobasic acid anion, and at the same time hydroxyl ions would be set free which would have a greater conductivity than the anion destroyed. The molecular conductivity at infinite dilution would then be too great, but this would be counterbalanced by the increase of the molecular conductivity at each dilution. The effect of hydrolysis on the value of the dissocciation constant might then be nullified, or at least partially obscured. If the amount hydrolyzed at each dilution increased over the amount hydrolyzed at each preceding dilution, as is probably the case, the value of the constant as obtained by Rudolphi's dilution formula might remain approximately the same.

According to a rule already mentioned, the strength of the second carboxyl group decreases as the dissociation constant increases, and therefore the sodium salts of acids with high dissociation constants would hydrolyze more easily than those of acids with low dissociation constants, more particularly at low dilutions. From these considerations we may deduce that, if the affinity constant of the acid is high, the value of K for the sodium salt as calculated by Rudolphi's formula would be more constant than the value for the salt of an acid the affinity constant of which is low.

This deduction is not negatived by the results obtained nor is it definitely proven, though the salts of the normal alkyl substituted derivatives seem to bear it out. That these salts do not act strictly in accordance with this rule finds an analogy in other measurements. Hjelt* observed that though methyl and di-methyl malonic acids have approximately the same affinity constants, in reference to the facility with which they are formed from their esters they stand far away from one another.

In the following table col. 1 contains the increase in molecular conductivity when the dilution is increased from 32 to 64 litres, col. 2, the increase from 64 to 128 litres, and so on for dilutions up to 2048 litres.

Table 8.

The increase with dilution in the molecular conductivities of the di-sodium salts of the acids.

Acid.	(1).	(2).	(3).	(4).	(5).	(6).
N-Propyl Malonic.	11.0	10.1	7.5	2.7	2.0	2.4
I-Propyl Malonic.	9.6	8.4	7.5	5.7	4.3	4.1
I-Butyl Malonic.	10.6	13.1	8.0	3.8	4.7	2.2
I-Amyl Malonic.	11.1	7.0	5.5	7.2	2.5	6.0
Di-Methyl Malonic.	10.2	11.2	5.5	6.0	4.5	1.3
Di-Ethyl Malonic.	15.2	8.8	6.7	5.5	4.3	5.5
Di-Propyl Malonic.	---	9.5	4.3	8.0	4.5	3.7
Di-I-Butyl Malonic.	---	13.5	8.0	11.3	9.2	4.4
Methyl N-Propyl Malonic.	---	9.7	9.4	8.4	6.7	5.9
Methyl I-Propyl Malonic.	---	14.6	10.9	9.4	11.4	---
Methyl N-Butyl Malonic.	---	9.8	5.6	6.0	6.0	---
Methyl I-Butyl Malonic.	---	21.4	6.9	9.0	7.5	16.0
Methyl I-Amyl Malonic.	---	12.7	8.4	6.1	4.3	5.1
Ethyl N-Propyl Malonic.	10.3	11.3	10.0	9.3	5.0	5.5
Ethyl I-Propyl Malonic.	---	12.7	8.3	7.0	7.5	7.0
Ethyl N-Butyl Malonic.	---	10.4	8.8	10.5	6.0	6.2
Ethyl I-Butyl Malonic.	---	9.6	10.5	7.6	7.9	7.9
Ethyl I-Amyl Malonic.	---	qu.u	8.9	10.1	4.5	4.0

An examination of these results show that of the sodium salts of the mono-alkyl substituted malonic acids, only the iso-propyl and the iso-amyl derivatives are appreciably hydrolyzed, the former to a slight extent, the latter very distinctly. The derivatives of all the di-alkyl substituted acids are hydrolyzed, with the single exception of Di-sodium di-methyl malonate. It is worthy of note that di-methyl malonic acid has the lowest dissociation constant of all the acids of the malonic series, and that consequently the acid character of its second carboxyl group is the strongest in the series.

The salts of acids containing groups of iso- structure are hydrolyzed to a greater extent than those containing normal groups but otherwise similar in constitution.

Table 9.

N-Propyl Malonic.	2.7
I-Propyl Malonic.	4.7 .
MethylN-Butyl Malonic.	6.0
Methyl I-Butyl Malonic.	10.8
Methyl N-Propyl Malonic.	7.0
Methyl I-Propyl Malonic.	10.4
Ethyl N-Propyl Malonic.	6.6
Ethyl I-Propyl Malonic.	7.2

Ethyl N-Butyl Malonic.	7.6
Ethyl I-Butyl Malonic.	7.8

The numbers given are the average increases in molecular conductivities for the three final values of the dilutions for each acid.They show that the iso- groups have the greatest effects on the hydrolysis when they are substituted together with the methyl group.The effects due to the same groups when substituted with the ethyl group are not so obvious,the methyl group probably causing greater steric interference and rendering the molecule more unstable.

Dr Walker pointed out that the hydrolysis of the di-metallic salts might have been expected since experiments done by him on the strychnine salts of various aliphatic acids,showed that even mono-basic acids of normal structure and of only moderate complexity formed only the acid salt with strychnine,or in cases where the normal salts were formed,they proved to be very unstable in the presence of water.With dibasic acids only the acid salt would form.

Ionic Conductivities.

In finding the molecular conductivities of the acids at infinite dilution use was made of the numbers found for the limiting conductivities of their mono-sodium salts.From these the conductivity of the sodium ion, 49.3,was subtracted and the conductivity of the hydrogen ion, 325,added on.*

From the limiting molecular conductivities of the two classes of sodium salts the ionic conductivities of the corresponding anions,the mono-basic and the di-basic,were found by subtracting the conductivity of the sodium ion.Owing to the great variation in molecular conductivity at high dilutions the results for the neutral anions are only roughly approximate,but they serve to indicate in some cases the relative conductivities.Theoretically, a symmetrical di-basic ion should carry twice the quantity of electricity carried by a mono-basic ion of similar constitution, and in the malonic acids this should be very approximately true, provided that the additional hydrogen atom in the mono-basic ion affected its conductance only by slightly increasing its mass.In the table on the following page,A is the ionic conductivity of the acid anion,N the conductivity of the neutral ion and E the excess of N over the theoretical value.

Table 10.

Ionic Conductivities.

Acid.	A.	N.	E.
N-Propyl Malonic.	44	86	—
Iso-Propyl Malonic.	43	88	—
Iso-Butyl Malonic.	41	88	—
Iso-Amyl Malonic.	42	84	—
Di-Methyl Malonic.	44	93	—
Di-Ethyl Malonic.	34	103	35
Di-Propyl Malonic.	35	84	14
Di-Iso-Butyl Malonic.	47	95	—
Methyl N-Propyl Malonic.	32	103	39
Methyl Iso-Propyl Malonic.	33	101	35
Methyl N-Butyl Malonic.	24	105	57
Methyl Iso-Butyl Malonic.	27	100	46
Methyl Iso-Amyl Malonic.	30	96	36
Ethyl N-Propyl Malonic.	40	103	23
Ethyl Iso-Propyl Malonic.	39	104	26
Ethyl N-Butyl Malonic.	31	101	39
Ethyl Iso-Butyl Malonic.	29	106	48
Ethyl Iso-Amyl Malonic.	30	94	34

Dissociation Constants of the Malonic Acids.

In the following table the dissociation constants of the alkyl substituted malonic acids are summarized. Those acids which are of similar structure are grouped together in the order of increasing molecular weight. Such an arrangement make plain certain regularities in the variations of the constants depending on the nature of the substituting groups.

Table 11.

(1) Acid.	Mol.Wt.	$KX10^5$.
N-Propyl Malonic.	146	0.111
Methyl N-Propyl Malonic.	160	0.212
Ethyl N-Propyl Malonic.	174	1.106

(2). Acid	Mol.Wt.	$KX10^5$.
Iso-Propyl Malonic.	146	0.130
Methyl Iso-Propyl Malonic.	160	0.145
Ethyl Iso-Propyl Malonic.	174	0.254

(3).Acid.	Mol.Wt.	$KX10^{5}$.
Iso-Butyl Malonic.	160	0.096
Methyl Iso-Butyl Malonic.	174	0.368
Ethyl Iso-Butyl Malonic.	188	1.904

(4).Acid.	Mol.Wt.	$KX10^{5}$
Iso-Amyl Malonic.	174	0.126
Methyl Iso-Amyl Malonic.	188	0.218
Ethyl Iso-Amyl Malonic.	202	1.053

(5).Acid.	Mol.Wt.	$KX10^{5}$.
Methyl N-Butyl Malonic.	174	0.175
Ethyl N-Butyl Malonic.	188	1.166

(6).Acid.	Mol.Wt.	$KX10^{5}$.
Di-Methyl Malonic.	132	0.077
Di-Ethyl Malonic.	160	0.751
Di-Propyl Malonic.	188	1.194

(7).Acid.	Mol.Wt.	$KX10^{5}$.
Di-Iso-Butyl Malonic.	216	0.142

(8).Acid.	Mol.Wt.	KX10^5.
Malonic.*	104	0.158
Methyl Malonic.*	118	0.087
Di-Methyl Malonic.	132	0.077
Methyl Ethyl Malonic.	146	0.161
Methyl N-Propyl Malonic.	160	0.212
Methyl N-Butyl Malonic.	174	0.175

(9).Acid.	Mol.Wt.	KX10^5.
Malonic.	104	0.158
Ethyl Malonic.*	132	0.127
Ethyl Methyl Malonic.	146	0.161
Di-Ethyl Malonic.	160	0.751
Ethyl N-Propyl Malonic.	174	1.106
Ethyl N-Butyl Malonic.	188	1.166

(10).Acid.	Mol.Wt.	KX10^5.
Methyl Iso-Propyl Malonic.	160	0.145
Methyl Iso-Butyl Malonic.	174	0.369
Methyl Iso-Amyl Malonic.	188	0.218

(11).Acid.	Mol.Wt.	$K \times 10^5$.
Ethyl Iso-Propyl Malonic.	174	0.254
Ethyl Iso-Butyl Malonic.	188	1.904
Ethyl Iso-Amyl Malonic.	202	1.053

A study of the results in the above groups enables us to draw certain definite conclusions regarding the cause of variations in the dissociation constants.That the increase in the dissociation constant is not a simple function of the molecular weight,even when analogous acids are considered,is shown clearly by the variation of the constant in the first five groups above.It is evident from these that the ethyl group has a much greater effect on the conductivity than the methyl group.This is even more clearly shown by group (8).By the introduction of one methyl group the dissociation constant of malonic acid is reduced by almost one-half;the introduction of a second methyl group causes a further decrease which however is only slight,the approximation of two groups to the central carbon atom having an influence opposite to the influence of the chemical nature of the methyl group. When one of the methyl groups is substituted by an ethyl group there is a decided increase in the constant which is further increased by the substitution of a normal propyl or a normal butyl group.

Group (9) admits of similar deductions.Here however the normal butyl group is seen to have a greater effect than the normal propyl group.The effects of the two are,in both group (8) and group (9),almost the same.

The alkyl radicals of iso- structure invariably have a greater effect than the isomeric radicals of normal structure. The iso-butyl group when substituted alone causes a greater depression of the conductivity than either the iso-propyl or the iso-amyl groups.In the di-substituted acids the reverse is the case,the iso-butyl group causing the greatest elevation of the three.

The results in group (6) indicate that the propyl radical, when substituted with a second radical has a greater effect in increasing the constant than the ethyl radical has.This suggests that the great differences between the dissociation constants of di-substituted acids containing methyl and the constants of the similar acids containing ethyl,must be due to the depressing effect of the methyl group opposing the elevating effect of the second substituting radical.

The results obtained seem to indicate that differences in the spacial arrangements of the molecules exercise a considerable influence on the dissociation of the malonic acids.The acids containing iso- groups are in general dissociated to a greater extent than the isomeric acids containing normal groups.e.g.:--

Acid.	$KX10^5$.
Normal Propyl Malonic.	0.111
Iso-Propyl Malonic.	0.130
Ethyl Normal Butyl Malonic.	1.166
Ethyl Iso-Butyl Malonic.	1.904

Di-alkyl substituted acids are dissociated more than the isomeric mono-alkyl derivatives. e.g.:--

Acid.	$KX10^5$
Iso-Amyl Malonic.	0.126
Ethyl Normal Propyl Malonic.	1.106
Methyl Iso-Butyl Malonic.	0.369

A more decisive indication than either of these is noticed in the case of the di-ethyl and di-propyl malonic acids.The introduction of a single ethyl group causes a slight decrease in the value of the dissociation constant; the introduction of a second ethyl group causes a relatively great increase.The propyl group acts similarly.As has already been pointed out,methyl first causes a great decrease in the value of the constant and then an additional slight decrease.

This leads to the following conclusion.---The introduction of an alkyl group into malonic acid is attended by a fall in the value of the dissociation constant.The introduction of a second alkyl group tends to lower the value of the constant still further but this tendency is more than counterbalanced by an opposing influence due to the position of the alkyl groups in the molecule.This statement holds true no matter what alkyl groups are considered,though in the case of the methyl group the tendency to lower the value of the constant is not overcome by the influence due to spacial arrangement.

That the acid character of one carboxyl increases while that of the other decreases as the alkyl substituents become more complex,is evident from the results showing the hydrolysis of the di-sodium salts and from the affinity constants of the acids themselves.

In conclsion I wish to express my thanks to Dr Walker for help and advice,and my appreciation of the interest he has shown throughout the research.

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