CCXIV.—*Studies in Complex Salts. Part III. The Effect of Alkyl Substitution on the Stability of the Dimalonatocupriate Ion.*

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Modern views on the electronic constitution of complex ions, although satisfactory from a purely stoicheiometric standpoint, give little information as to the causes underlying the large variation in stability of these ions. The suggestion that the stability of complex ions depends to a great extent upon the degree of localisation of negative poles in the donor ions or molecules has already been put forward in Part I of this series (J., 1928, 2985). It has also been pointed out that probably there is some fundamental connexion between the extent of the electrolytic dissociation of a simple molecule in aqueous solution and that of the corresponding complex ion (Riley and Fisher, J., 1929, 2006). In Part II of this series (J., 1929, 1307), evidence was obtained that the relative stability of the bisdicarboxylatocupriate ions was dependent upon the number of CH_2 groups between the two carboxyl groups. This is, of course, in accordance with an extension of Baeyer's strain hypothesis to chelate rings, but it might equally well be interpreted on a polar hypothesis. Both effects probably play an important part in determining the stability, but the writer is of the opinion that the polar effect is the dominant one in the compounds studied. This view is based upon the following considerations. Sodium formate and sodium acetate when added to copper sulphate solution have little effect upon the concentration of the copper ions, as determined by the potentiometric method described in Part II (*loc. cit.*). The oxalate ion forms a large number of very stable complex salts, and the primary cause for this must surely be the mutual effect of the two C_2O_4 groups. This effect will be damped by the interposition of CH_2 groups between the two carboxyl groups, thus explaining the decreasing tendency of the malonate and succinate ions to co-ordinate with copper.

With the view further to elucidate the factors which govern the degree of dissociation of complex ions in aqueous solution, a study has been made, by a potentiometric method, of the effect of alkyl substitution on the stability of the copper–malonate complex.

EXPERIMENTAL.

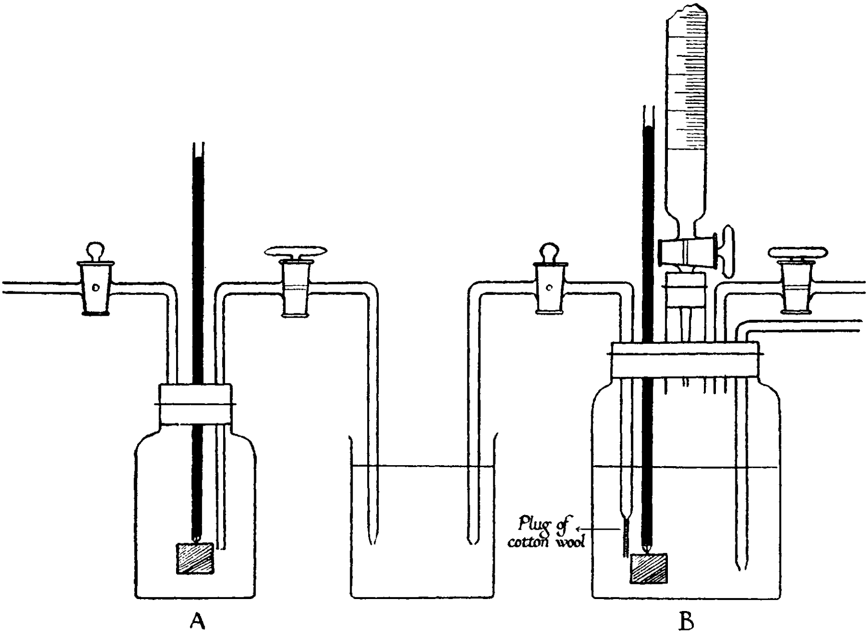
It was shown in Part II that the potential of the concentration cell $Cu|0{\cdot}01M\text{-}CuSO_4|$Satd. $KNO_3|0{\cdot}01M\text{-}CuSO_4 + 0{\cdot}03M\text{-}CH_2(CO_2Na)_2|Cu$ falls at first and after several hours attains a constant value. This initial fall is probably due to the action of the malonate on the copper electrode in the presence of a minute trace of oxygen. Whereas a freshly plated copper electrode will remain bright in a well boiled-out solution of copper sulphate over a period of several months, without showing any appreciable alteration in potential, an electrode in a similarly prepared solution to which sodium malonate has been added changes colour rapidly, becoming yellowish after a few hours, then gradually reddish-brown, and finally, after several weeks, almost black. The rate of this change in the appearance of the electrode was found to vary considerably with the various substituted malonates used in this investigation, being slowest for the *iso*propylmalonate and most rapid for the disubstituted malonates. With sodium *iso*propylmalonate a steady potential was quickly established, whereas with the diethyl- and dipropyl-malonates the potential of the concentration cell fell continuously over several days, in some experiments to zero, and it was found impossible to obtain concordant steady potentials. In view of the above, it seems highly probable that the initial fall is due to some change in the nature of the electrode surface, and that the correct measure of the copper-ion concentration is the potential of the concentration cell, established immediately the electrode is dipped into the solution. This view is supported by the fact that the darkened electrodes on immersion in fresh $0{\cdot}01M$-copper sulphate solution were positively charged to the extent of 10—30 millivolts compared with a freshly plated electrode in the same solution.

Several experiments were made with the object of preventing this initial fall in the potential of the concentration cells, but with little success. Thorough boiling out of all the solutions used, even in a current of hydrogen, and the addition of 2% of alcohol to the electrode solutions were all equally ineffective.

A preliminary investigation of the solubility of the normal copper salts of the various substituted malonic acids indicated that a possible solution of this experimental difficulty was to carry out the determinations of the copper-ion concentration by a potentiometric titration method. The time occupied in such experiments would be insufficient for there to be any great action upon the electrode surface, provided precautions were taken to exclude dissolved oxygen from the solutions used. Concordant values were obtained by the method now described.

Potentiometer.—The potentiometer used consisted of a Kohlrausch wheel bridge, approximately 3 m. long. A Weston cell (*P.D.* 1·0182 volts) was used as standard, and the zero point was determined by means of a capillary electrometer. In determining the potential of the concentration cell, the cell was connected in series with the Weston cell and its potential could be read accurately to within 0·5 millivolt. All measurements were made at room temperature.

FIG. 1.



Concentration Cell.—The arrangement of the concentration cell is shown in Fig. 1. It consists of a small bottle A, of about 40 c.c. capacity, fitted with syphon tubes and an electrode. The other half-element, B, is a 100 c.c. bottle, provided with a stopper carrying the electrode, a burette, inlet and outlet tubes for hydrogen, and a connecting tube filled with saturated potassium nitrate and plugged with cotton wool. Measurements were made with the tap of this tube closed but well wetted with the potassium nitrate solution.

Electrodes.—The electrodes used in the half-elements were made by connecting 1 sq. inch of pure copper foil to a platinum wire sealed through a glass tube. After being etched with nitric acid, the electrodes were heavily plated in the manner described in Part II, and before use in each experiment, they were re-plated over-night, allowed to remain short-circuited in the bath for 24 hours, and then well washed with boiled-out water, dried with filter paper, and introduced into the half-elements as quickly as possible.

Copper Sulphate.—Finely powdered, air-dried, " reagent " copper sulphate was used.

Water.—Distilled water, previously boiled-out over-night, was boiled in a current of hydrogen for 4 hours, rapidly cooled in a current of hydrogen, and used immediately.

Sodium Salts.—The sodium salts of malonic and the substituted malonic acids were prepared from the pure acids, which were purchased and carefully recrystallised where necessary, by adding an exactly equivalent quantity of freshly prepared, standardised carbonate-free caustic soda solution. After the solution had been filtered and evaporated almost to dryness, the sodium salt was precipitated by the addition of absolute alcohol, filtered off, well washed with absolute alcohol, and redissolved in water, the process being repeated. It was then dried, finely powdered, thoroughly dried for six hours at 120—130°, allowed to cool over phosphorus pentoxide, and the quantity required for the titration immediately weighed out. The purity of the product was tested by determining the quantity of sodium present, all the results being in excellent agreement with those required by theory.

Procedure.—Into a 50-c.c. graduated flask was weighed out exactly 0·015 g.-mol. (*i.e.*, sufficient to form 50 c.c. of a $0{\cdot}3M$-solution) of the pure dry sodium salt of the malonic acid under consideration, which was then dissolved in a small quantity of water. 0·0005 G.-mol. (*i.e.*, 0·125 g., sufficient to form 50 c.c. of a $0{\cdot}01M$-solution) of copper sulphate was dissolved in a little water, and the solution added to that of the sodium salt, the whole being diluted to exactly 50 c.c. Meanwhile, 250 c.c. of a $0{\cdot}01M$-solution of copper sulphate had been prepared. The half-element A was filled with the latter solution and exactly 50 c.c. of the same solution were run into B. A fairly rapid current of hydrogen was passed through the solution in B for a few minutes, and the potential of the concentration cell read. This was in each experiment zero. The malonate–copper sulphate solution was then run into B from the burette, the potential of the concentration cell being read at convenient intervals. Stirring was effected by means of the current of hydrogen, which was stopped during the actual measurement. A slight drop in potential is caused by bubbling hydrogen through the solution, but this rises again to its original value as soon as the current is stopped. Except in the case of the diethyl- and dipropyl-malonates, steady potentials were established at once during the earlier part of the titration, a few minutes being necessary for the establishment of equilibrium for the last two or three readings. On completion of the titration, which occupied about an hour, the solution in B was removed, and after being rinsed the half-element was again filled with 0·01*M*-copper sulphate. The concentration cell then showed a negative potential of 2—10 millivolts which slowly fell, becoming zero again in the course of 30—40 minutes. This shows that no serious alteration in the nature of the electrode surface had occurred during the titration. A slight change in colour, which it was impossible to prevent, had, however, taken place. Whereas the electrode in A retained its original salmon-red colour, that in B developed a slight yellowish tint. Nevertheless, the effect of this change in the colour of the electrode can only be small, and although it is impossible to be certain as to the fundamental accuracy of the results recorded, there can be little doubt that they are relatively correct.

In order to determine whether or not the presence of dissolved hydrogen had any appreciable effect upon the electrode potentials, some preliminary experiments were carried out with sodium malonate, the water used having been previously well boiled-out but not saturated with hydrogen. The results obtained are given in Table I: they are typical of the concordance which can be obtained in consecutive experiments by taking the precautions outlined above. Although it is possible to obtain concordant values without the use of hydrogen, occasionally much lower values were obtained, for no apparent reason, and it was therefore deemed advisable to use hydrogen for the titrations with the substituted malonic acids. In the tables of results, the constants of instability, $K = [Cu^{\cdot\cdot}][X'']^2/[CuX_2'']$, are calculated upon the same assumptions as those mentioned in Part II. The values of *K* increase slowly with increase in the concentration of the sodium malonates, doubtless owing to the incomplete dissociation of the sodium salts at the dilutions under consideration: these degrees of dissociation being unknown, it is impossible to apply a correction for this factor.

TABLE I.

Conc. of malonate, millimols./litre	0·0	3·0	5·9	8·7	11·5	14·3	17·0	19·6	22·2	27·3	32·1	41·4	50·0	58·1	72·7	85·7	100·0
P.D., millivolts (in hydrogen)	0	2	9	19	37	53	65	76	87	100	108	117	125	129	138	144	149
P.D., millivolts (in air)	0	3	9	19	38	55	68	80	91	104	111	120	126	130	137	142	146

Conc. of malonate, m.mols./l.	*P.D.*, milli-volts.	$[\mathrm{Cu}^{\cdot\cdot}] \times 10^7$.	$[\mathrm{CuX_2}''] \times 10^2$.	$[\mathrm{X}'']^2 \times 10^4$.	*K*,
		Sodium malonate.			
0·0	0	62900			
3·0	2	53700			
5·9	9	30800			
8·7	19	13900			
11·5	37	3330			
14·3	53	935			
17·0	65	361			
19·6	76	151			
22·2	87	62·9	0·999	0·0493	$0·31 \times 10^{-8}$
27·3	100	22·4	1·000	0·533	1·2
32·1	108	11·9	1·000	1·46	1·7
41·4	117	5·81	1·000	4·58	2·7
50·0	125	3·08	1·000	9·00	2·8
58·1	129	2·24	1·000	14·5	3·3
72·7	138	1·10	1·000	27·8	3·1
85·7	144	0·681	1·000	43·2	2·9
100·0	149	0·458	1·000	64·0	2·9
		Sodium methylmalonate.			
3·0	3	49600			
5·9	8	33300			
8·7	17	16300			
11·5	33	4580			
14·3	48	1390			
17·0	60	536			
19·6	70	243			
22·2	81	101	0·999	0·0493	$0·50 \times 10^{-8}$
27·3	95	33·3	1·000	0·533	1·8
32·1	104	16·3	1·000	1·46	2·4
41·4	115	6·81	1·000	4·58	3·1
50·0	122	3·91	1·000	9·00	3·5
58·1	126	2·84	1·000	14·5	4·1
72·7	133	1·63	1·000	27·8	4·5
85·7	136	1·29	1·000	43·2	5·6
100·0	140	0·979	1·000	64·0	6·3
		Sodium ethylmalonate.			
3·0	2	53700			
5·9	7	36100			
8·7	16	17700			
11·5	32	4960			
14·3	48	1390			
17·0	61	496			
19·6	72	207			
22·2	84	79·8	0·999	0·0493	$0·39 \times 10^{-8}$
27·3	98	26·3	1·000	0·533	1·4
32·1	106	13·9	1·000	1·46	2·0
41·4	117	5·81	1·000	4·58	2·7
50·0	124	3·33	1·000	9·00	3·0
58·1	129	2·24	1·000	14·5	3·3
72·7	134	1·51	1·000	27·8	4·2
85·7	138	1·10	1·000	43·2	4·8
100·0	142	0·798	1·000	64·0	5·1

Conc. of malonate, m.mols./l.	*P.D.*, milli-volts.	$[Cu^{\cdot\cdot}]\times 10^7$.	$[CuX_2'']\times 10^2$.	$[X'']^2\times 10^4$.	*K*.
		Sodium propylmalonate.			
3·0	2	53700			
5·9	6	39100			
8·7	15	19100			
11·5	30	5810			
14·3	44	1910			
17·0	56	737			
19·6	73	191			
22·2	84	79·8	0·999	0·0493	$0·39\times 10^{-8}$
27·3	95	33·3	1·000	0·533	1·8
32·1	103	17·7	1·000	1·46	2·6
41·4	110	10·1	1·000	4·58	4·6
50·0	115	6·81	1·000	9·00	6·1
58·1	121	4·23	1·000	14·5	6·1
72·7	130	2·07	1·000	27·8	5·8
85·7	134	1·51	1·000	43·2	6·5
100·0	138	1·10	1·000	64·0	7·0
		Sodium iso*propylmalonate.*			
3·0	2	53700			
5·9	8	33300			
8·7	18	15100			
11·5	33	4580			
14·3	50	1190			
17·0	68	284			
19·6	88	58·1			
22·2	107	12·9	1·000	0·0484	$0·62\times 10^{-9}$
27·3	129	2·24	1·000	0·533	1·2
32·1	141	0·864	1·000	1·46	1·3
41·4	155	0·284	1·000	4·58	1·3
50·0	163	0·151	1·000	9·00	1·4
58·1	168	0·101	1·000	14·5	1·5
72·7	174	0·0629	1·000	27·8	1·8
85·7	179	0·0423	1·000	43·2	1·8
100·0	183	0·0308	1·000	64·0	2·0
		Sodium dimethylmalonate.			
3·0	0	62900			
5·9	4	45800			
8·7	10	28400			
11·5	20	12900			
14·3	33	4580			
17·0	41	2420			
19·6	47	1510			
22·2	50	1190	0·988	0·0595	$0·072\times 10^{-6}$
27·3	56	737	0·993	0·554	0·41
32·1	62	458	0·995	1·49	0·69
41·4	70	243	0·998	4·60	1·12
50·0	75	163	0·998	9·02	1·5
58·1	80	110	0·999	14·5	1·6
72·7	87	62·9	0·999	27·8	1·8
85·7	92	42·3	1·000	43·2	1·8
100·0	96	30·8	1·000	64·0	2·0

Conc. of malonate, m.mols./l.	*P.D.*, milli-volts.	$[\mathrm{Cu}^{\cdot\cdot}] \times 10^7$.	$[\mathrm{CuX_2}''] \times 10^2$.	$[\mathrm{X}'']^2 \times 10^4$.	*K*.
		Sodium diethylmalonate.			
3·0	−3	79800			
5·9	0	62900			
8·7	4	45800			
11·5	10	28400			
14·3	15	19100			
17·0	14	20700			
19·6	15	19100			
22·2	19	13900	0·861	0·248	$0{\cdot}40 \times 10^{-5}$
27·3	25	8640	0·914	0·814	0·77
32·1	30	5810	0·942	1·76	1·1
41·4	40	2630	0·974	4·80	1·3
50·0	45	1770	0·982	9·22	1·7
58·1	49	1290	0·987	14·7	1·9
72·7	56	737	0·993	27·9	2·1
85·7	61	496	0·995	43·3	2·2
100·0	66	333	0·997	64·1	2·1
		Sodium dipropylmalonate.			
3·0	−2	73700			
5·9	0	62900			
8·7	5	42300			
11·5	13	22400			
14·3	22	11000			
17·0	5	42300			
19·6	2	53700			
22·2	9	30800	0·692	0·699	$0{\cdot}31 \times 10^{-5}$
27·3	22	11000	0·890	0·903	1·1
32·1	30	5810	0·942	1·76	1·1
41·4	38	3080	0·969	4·85	1·5
50·0	42	2240	0·978	9·27	2·1
58·1	46	1630	0·984	14·8	2·5
72·7	52	1010	0·990	28·0	2·9
85·7	55	798	0·992	43·4	3·5
100·0	59	581	0·994	64·2	3·8

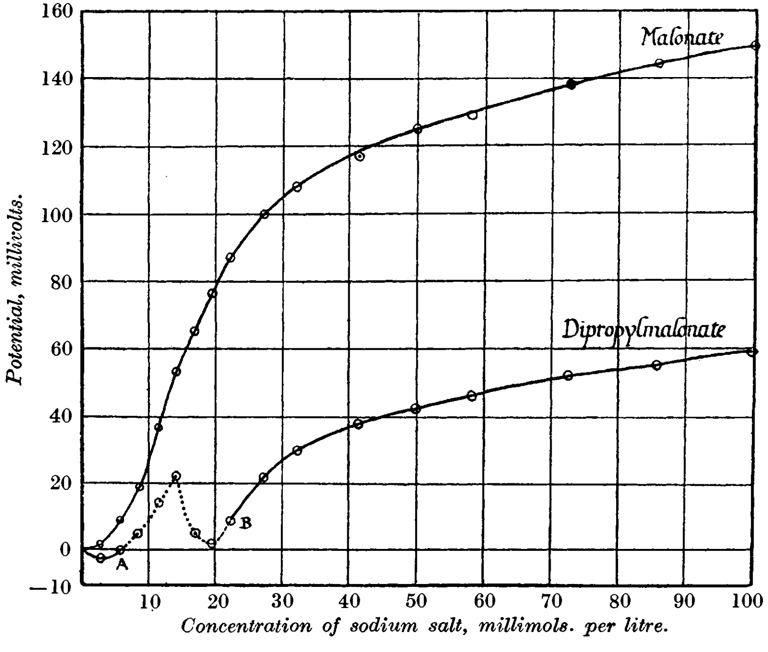
The total concentration of copper present in B is constant throughout the titration. Fig. 2 shows the change of potential of the concentration cell with change of concentration of the sodium salt for the malonate and the dipropylmalonate. The former is typical of the monosubstituted and dimethylmalonic acids, and the latter is similar to the curve for the diethylmalonic acid. The following is believed to be the interpretation of the curves. The addition of sodium malonate to the copper sulphate in the early stages of the titration brings about the reaction $\mathrm{CuSO_4 + CH_2(CO_2Na)_2 \rightleftarrows Na_2SO_4 + CH_2(CO_2)_2Cu}$. The copper malonate formed is not so highly dissociated as the copper sulphate (J., 1929, 2006), so there is a consequent diminution in the copper-ion concentration. As the amount of malonate is increased, the following reaction comes into play :

$$\mathrm{CH_2{<}{\overset{CO_2}{\underset{CO_2}{}}}{>}Cu + CH_2{<}{\overset{CO_2Na}{\underset{CO_2Na}{}}} \rightleftarrows Na_2[Cu(CH_2{\cdot}C_2O_4)_2]}$$

with a much more rapid diminution in the copper-ion concentration. All the curves show a point of inflexion at a concentration of the sodium salt of about 0·01*M*.

The sodium salts of diethyl- and dipropyl-malonic acids give a different type of curve. The initial increase in the copper-ion concentration is probably due to the greater degree of dissociation of the normal copper salts compared with copper sulphate. The subsequent increase in the potential of the cell is accompanied by the development of a faint turbidity in the solution. The potentials established at the points between *A* and *B* on the curve are not steady, but fall rapidly, and the shape of that part of the curve depends upon how quickly the readings are taken. Those recorded were measured in a similar manner to that employed in the case of the monosubstituted acids. The following is the probable explanation of this behaviour. The sodium salts of the two acids are slightly hydrolysed and the concentration of hydroxyl ions in the early part of the titration is sufficient to cause the separation of either copper hydroxide or some basic salt, partly as a colloid and partly as a precipitate. This causes a rapid diminution in the copper-ion concentration. As the addition of the sodium salt

FIG. 2.



proceeds, it reacts slowly with the precipitated hydroxide, causing an increase in the copper-ion concentration. Although the part of the curve between the points *A* and *B* is not reproducible, the subsequent portion of the curve is.

Discussion.

The above results indicate that the substitution of the groups methyl, ethyl, and propyl in the malonate ion has little effect upon its tendency to co-ordinate with copper, a slight decrease having been observed. The *iso*propyl group causes a comparatively large increase in the stability of the complex. This effect is probably a polar one, and it is interesting to note that the condensation of a second *iso*propyl group with malonic acid has not been effected. Both these phenomena would be explained by the migration of electrons from the *iso*propyl group. The substitution of two methyl groups causes a comparatively large decrease in the tendency of the ion to co-ordinate with the copper ion, and the substitution of two ethyl groups causes a still further decrease in this tendency. The effect of two propyl groups is approximately the same as that of two ethyl groups. If the stability of a complex ion depends upon the degree of localisation of negative poles in the donor ion, then this phenomenon must be due to the decrease of the charge on the carboxyl oxygen atoms brought about by the apparent reversal, in the free ion, of the usual polarity of the alkyl groups concerned. It is also noteworthy that the effect of dialkyl substitution is opposite to that which would be anticipated were strain the important factor in determining the stability of the complex.

Certain other properties can be correlated with this alteration in the tendency to co-ordinate with copper. Mention has already been made of the hydrolysis noticed during the titration with sodium diethyl- and dipropyl-malonates. On warming the solution used for the titration, *i.e.*, $0{\cdot}3M$ with respect to the sodium salt and $0{\cdot}01M$ with respect to the copper sulphate, the extent of the hydrolysis was greatly increased and a greenish-brown precipitate was thrown down, the deep blue solution becoming green. This hydrolysis occurred most readily in the case of the dipropylmalonate, readily with the diethyl-, less readily with the dimethyl-, and only on prolonged boiling and to a very slight extent in the case of methyl-, ethyl-, and propyl-malonates. It was absent with the normal malonate and with the *iso*propylmalonate.

A study of the normal copper salts of the substituted malonic acids is in progress with the object of determining whether there is any connexion between the dissociation of the normal salts and that of the corresponding complex salts. It is, however, interesting to compare the change in colour of the normal salt, brought about by alkyl substitution, with the tendency of the corresponding ion to co-ordinate with copper as measured by the instability constant K.

TABLE II.

Malonic acid.	K.	Colour of normal Cu salt.	Behaviour of soltn. of Cu salt on boiling.
Unsubstituted	1×10^{-8}	Pale blue	Stable
Methyl	1×10^{-8}	Pale blue	Stable
Ethyl	1×10^{-8}	Pale blue	Stable
Propyl	1×10^{-8}	Pale blue	Stable
*iso*Propyl	1×10^{-9}	Very deep blue	Stable
Dimethyl	$0{\cdot}4 \times 10^{-6}$	Very deep blue	Hydrolysed
Diethyl	1×10^{-5}	Green	Hydrolysed
Dipropyl	1×10^{-5}	Green	Hydrolysed

It is obvious from Table II that the differences in the potentiometric behaviour of the various sodium salts indicate some fundamental change in the electronic constitution of the ions.

The primary and secondary dissociation constants of the same series of malonic acids have been determined by Gane and Ingold (J., 1929, 1691), and it is noteworthy that the values for K_1 and K_2 obtained by them indicate a large effect in the case of the dipropyl and the diethyl acids but only small effects in the case of the other acids.

Summary.

A method is described for determining the effect of the addition of the malonate and various substituted malonate ions on the copper-ion concentration in a solution of copper sulphate. The results indicate that the substitution of the groups methyl, ethyl, and propyl have little effect on the tendency of the malonate ion to co-ordinate with the copper ion, a small decrease having been observed. The *iso*propyl group causes a relatively large increase in this tendency, the dimethyl group a decrease, and the diethyl and dipropyl groups a still larger and approximately equal decrease.

These effects are correlated with certain other properties.

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