236. *Studies in Complex Salts. Part V. The Effect of Di*iso*propyl Substitution on the Stability of the Dimalonatocupriate Ion.*

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IT has already been shown (Part III; Riley, J., 1930, 1642) that, whereas substitution of the groups CH_3, C_2H_5, or n-C_3H_7 causes a slight decrease in the tendency of the malonate ion to co-ordinate with copper, the *iso*propyl group brings about a decided increase. Dialkyl substitution, it was also shown, in the case of dimethyl, diethyl, and di-n-propyl, brings about a pronounced decrease in this property. In view of the different behaviour of one *iso*propyl group, compared with the other alkyl groups, and of the pronounced effect of dialkyl substitution, a study of the effect of substituting two *iso*propyl groups in the malonate ion appeared to be highly desirable. Unfortunately at that time, the preparation of di*iso*-propylmalonic acid had not been described, and the suggested interpretation of the behaviour of the single *iso*propyl group indicated that it would be either impossible, or very difficult, to condense a second *iso*propyl group with malonic acid. Subsequently, however, Marshall (J., 1930, 2754; 1931, 2336) succeeded in preparing the required acid, but the difficulty he encountered amply confirmed our expectations. The authors are indebted to Dr. Marshall for 8 g. of the acid, with which they have studied the tendency of the di*iso*propylmalonate ion to co-ordinate with copper. The electrolytic dissociations of copper di*iso*propylmalonate and of di*iso*propylmalonic acid itself, in aqueous solution, have also been studied. The significance of the results is discussed later.

EXPERIMENTAL.

The potentiometric titration, employing sodium di*iso*propyl-malonate, was carried out in an exactly similar manner to that already described in Part III (*loc. cit.*). *Sodium di*iso*propylmalonate* was prepared by adding an exactly equivalent quantity of standard, carbonate-free, "A.R." caustic soda solution to the acid and evaporating the solution to small bulk in a platinum basin on the steam-bath. Unlike the sodium salts of malonic acid and the alkyl-malonic acids already studied, this salt was not precipitated by addition of absolute alcohol to the concentrated aqueous solution. Acetone, however, effected this precipitation. The precipitated sodium salt was dissolved in water, and the filtered solution again evaporated and precipitated with pure acetone. This process was repeated a third time, and the resulting sodium salt filtered, washed

with acetone, and dried at 120° for several hours before use (Found : Na, 19·83. $C_9H_{14}O_4Na_2$ requires Na, 19·89%). During the course of the titration, a slight turbidity developed in the copper malonate half-element, probably due to the hydrolysis of the normal copper salt. An aqueous solution of copper di*iso*propylmalonate was subsequently shown to be slightly hydrolysed in dilute aqueous solution. The concentrations of copper ions were calculated from the potentials of the concentration cell and the constant of instability of the bisdi*iso*propylmalonato-ion calculated in an exactly similar manner to that already described in Part III. The results obtained are shown in Table I.

TABLE I.

Instability constant of complex ion.

Conc. of malonate, m.-mols./l.	P.D., milli-volts.	$[Cu^{..}] \times 10^7$.	$[CuX_2''] \times 10^2$.	$[X''] \times 10^4$.	$K \times 10^7$.
0	0				
3·0	−2				
5·9	−1				
8·7	1				
11·5	7·5				
14·3	19				
17·0	31				
19·6	44				
22·2	56	737	0·993	0·0548	0·41
27·3	70	243	0·998	0·539	1·3
32·1	77	145	0·999	1·47	2·1
41·4	84	79·8	1·000	4·58	3·7
50·0	88	58·1	1·000	9·00	4·6
58·1	91	45·5	1·000	14·5	6·6
72·7	97	28·5	1·000	27·8	7·9
85·7	101	20·6	1·000	43·2	8·9
100·0	105	15·0	1·000	64·0	9·6

Preparation and Properties of Copper Diisopropylmalonate.— *Copper di*iso*propylmalonate* was prepared by digesting pure copper oxide with excess of the acid on the steam-bath for several hours. The resulting solution was filtered, the residue being thoroughly extracted with hot conductivity water, the extract added to the original solution, and the whole evaporated. The resulting copper salt, which was purified in the manner already described (Ives and Riley, J., 1931, 1998), was of a deep blue colour, deeper than copper malonate but not so deep as copper *iso*propylmalonate (Found : Cu, 25·3; C, 43·6; H, 5·5. $C_9H_{14}O_4Cu$ requires Cu, 25·5; C, 43·3; H, 5·6%). Like the diethyl and dipropyl salts, the di*iso*propyl salt is very readily hydrolysed; in fact, the dilute aqueous solutions of the salt used in the conductivity experiments are slightly turbid, indicating that some hydrolysis occurs even in the cold. The results obtained, which therefore should only be considered approx-

imate, are given in Table II, concentration being expressed as milli-equivs. per litre. It is assumed that the value of λ_0 is the same as that of copper dipropylmalonate, viz., 95·6.

TABLE II.

Dissociation constant of copper diisopropylmalonate.

Conc.	λ.	a.	$K \times 10^5$.	Conc.	λ.	a.	$K \times 10^5$.
3·751	6·9	0·0722	2·1	0·673	14·0	0·146	1·7
2·247	8·1	0·0847	1·8	0·509	16·0	0·167	1·7
1·428	9·6	0·100	1·6	0·497	16·4	0·172	1·8
1·189	11·1	0·116	1·8	0·361	19·0	0·199	1·8
0·943	12·1	0·127	1·7	—	95·6	—	—
0·738	13·2	0·138	1·6				

The results of the measurements of the conductivity of aqueous solutions of diisopropylmalonic acid are shown in Table III, concentrations being in millimols. per litre. The acid used was carefully purified by several recrystallisations from aqueous acetone. The results show that the acid behaves very similarly to the dipropyl

TABLE III.

Dissociation constant of diisopropylmalonic acid.

Conc.	μ.	a.	$K \times 10^3$.	Conc.	μ.	a.	$K \times 10^3$.
3·357	288·9	0·7414	7·14	0·722	345·8	0·8875	5·05
2·169	308·8	0·7925	6·57	0·405	353·6	0·9075	3·60
1·782	318·9	0·8184	6·57	0·206	356·3	0·9144	2·01
1·512	322·6	0·8279	6·02	—	389·65	—	—
1·081	333·1	0·8549	5·45				

acid. The values of K_1 have been calculated from the value 389·65 for λ_0 (Vogel, J., 1929, 1476); this can only be considered as approximate, for it was obtained from conductivity data of aqueous solutions of the sodium salt of dipropylmalonic acid, which are appreciably hydrolysed. No other method is available for the accurate determination of λ_0, for diisopropylmalonic acid is fairly " strong," and mobility and activity errors, introduced when extrapolation methods based on the dilution law are used, will be appreciable. The value of K_1 obtained by this method serves to compare it with the results obtained for the other alkylmalonic acids studied by Vogel (*loc. cit.*).

Discussion.

The varying effects of alkyl substitution on the stability of the malonatocupriate ion can now, it is believed, be simply explained. Although the dioxalatocupriate ion is considerably less dissociated ($K = 3 \times 10^{-11}$; J., 1931, 2033) than the dimalonatocupriate ion ($K = 10^{-8}$), this does not mean that a 5-membered chelate ring is necessarily less strained than a 6-membered. The cause of the greater stability of the oxalato-ring is probably due to the very

much greater localisation of the negative charges on the two carboxyl oxygen atoms, brought about by their mutual effect, this completely masking any instability brought about by strain in the chelate ring. Although there may be less strain in the malonato-chelate ring, its decreased stability can be accounted for by a diminution in the negative charge on the carboxyl oxygen atoms, due to the buffering action of the median CH_2 group. Let it be granted, then, that of all chelate rings of this type, the least strained is 6-membered (malonato), and further, that the distance apart of the two carboxyl groups in this ring of minimum strain lies somewhere between that in malonic acid and that in methylmalonic acid. The fact that methyl, ethyl, or n-propyl groups cause only a very slight decrease in the stability of the malonatocupriate complex indicates that diminution in the distance apart of the two carboxyl groups brought about by the substitution of these alkyl groups (according to the valency-deflexion theory of Ingold) with a consequent introduction of a slight amount of strain is more or less compensated by the polar effect of the alkyl group (this causing an increase of the negative charge on the carboxyl oxygen atom). The fact that the stabilities of the malonate and these alkylmalonate complexes are so nearly equal indicates that the chelate ring of minimum strain must have an intermediate structure. The stability of the *iso*propylmalonato-complex ($K = 10^{-9}$) indicates that the *iso*propyl group must have strong electron-repelling properties. In the disubstituted complexes, the effect of strain becomes obvious in reducing the stability of the complex. This is partially compensated in the dimethyl complex ($K = 0.4 \times 10^{-6}$) by the polar property of the methyl group. This compensatory effect is reduced in the diethyl and dipropyl complexes ($K = 10^{-5}$) owing to the buffering action of the methylene groups. It is very significant that the di*iso*propyl complex ($K = 10^{-7}$) is more stable than the dimethyl, again illustrating the stronger electron-repelling properties of the *iso*propyl group, compared with the other alkyl groups.

This simple explanation of the varying stability of these complexes, which involves only two factors, ring strain and the direct transmission of a polar effect, indicates that the potentiometric method of studying these problems gives results which can be more readily interpreted than those obtained from conductivity studies. Although di*iso*propylmalonic acid is in many ways different from the n-acid, conductivity measurements show that the primary dissociation constants of these two acids are approximately the same. This is probably due to the free negative pole, formed when the first hydrogen ion dissociates, influencing the rest of the molecule to a much greater extent than the two *iso*propyl groups.

3 M

The interpretation of the conductivity data of the normal copper salt is also complicated by the possibility of the dissociation occurring in two steps. This matter has been already discussed (Ives and Riley, *loc. cit.*). It is interesting to note the greater dissociation constant of the di*iso*propyl copper salt compared with those of the other disubstituted copper salts, particularly in view of the greater co-ordinating tendency of the former.