389. *The Dissociation Constants of the Cupric Salts of Some Monocarboxylic Acids.*

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The solubilities of cupric iodate in solutions of the sodium salts of seventeen monocarboxylic acids of the aliphatic and substituted aliphatic series have been used to calculate the dissociation constants of the equilibria $Cu^{++} + R^- \rightleftharpoons CuR^+$, where R^- represents the carboxylate anions. In general, the extent to which the polarities of substituent groups affect the dissociation constants of the acids is reflected in the values obtained for the dissociation constants of the copper salts. Glycollate and lactate are outstanding exceptions in that strong chelation occurs between their hydroxyl groups and cupric ions.

There is considerable information available concerning the extent to which complex formation takes place between metallic cations and dicarboxylate anions. Some of these results have been obtained from series designed to examine the effects of substitution or of increasing the chain lengths between the carboxyl groups. As instances of this, the results of Cannan and Kibrick (*J. Amer. Chem. Soc.*, 1938, **60**, 2314) and Topp and Davies (*J.*, 1940, 87) show that with the cations zinc, magnesium, calcium, strontium, and barium there is an increase in the dissociation constants of the complexes formed by a particular cation on passing along the series oxalate to adipate. This has been shown to be true also with some other cations with the oxalates and malonates (Money and Davies, *Trans. Faraday Soc.*, 1932, **28**, 609; Stock and Davies, *J.*, 1949, 1371). The replacement of hydrogen by other groups in the chain of a particular anion is a further variant which has been pursued, and again general trends are noticeable. For example, the data of Cannan and Kibrick (*loc. cit.*), and of Topp and Davies (*loc. cit.*) for the series succinic, malic, and DL-tartaric, show the result of introducing hydroxyl groups, while the results of Riley (*J.*, 1930, 1642) and of Ives and Riley (*J.*, 1931, 2006) indicate that alkyl substitution influences the dissociation constants of copper and zinc malonates.

With the monocarboxylates, the results available (*e.g.*, Cannan and Kibrick, *loc. cit.*; Topp and Davies, *loc. cit.*; Davies, *J.*, 1938, 277; Davies and Waind, *J.*, 1950, 301) indicate effects similar to those found with the dicarboxylates, but most of these results have been confined to zinc and the alkaline-earth metals. As extension to these, some results are given here for the cupric ion. These were obtained by passing solutions of sodium salts of the acids through saturators containing cupric iodate. The solutions were kept at a pH of about 4 by having an excess of the acid present. This precaution was necessary to avoid hydrolysis effects and the formation of basic salts.

Experimental.

Cupric iodate crystals were formed by allowing strong solutions of cupric sulphate and potassium iodate to drip slowly into nearly boiling water. The product was ground and the " fines " washed out. If the salt is precipitated in cold water, very fine crystals of high solubility are produced. The crystals were packed in saturators of the type described by Money and Davies (*J.*, 1934, 400), and the iodate concentrations of the saturated solutions (obtained at 25° ± 0·03°) were determined volumetrically by using sodium thiosulphate standardised by potassium iodate. Most of the acids used were of AnalaR or Kahlbaum quality. With those containing halogens, blank titrations were made; these, in general, showed that negligible corrections were necessary. A glass electrode was used to measure the pH of the saturated solutions.

Whilst in most cases the solubility in water was $3{\cdot}33 \times 10^{-3}$ M., there were a few instances, especially when a fresh batch of crystals was used, when slight variations from this were found. The solubility in water was therefore determined for each series.

If the reasonable assumption is made that $Cu(IO_3)^+$ has a dissociation constant of 0·15 (by analogy with similar iodates, Davies, *J.*, 1930, 2410; 1938, 271)—a factor which cannot introduce much error since the amount involved is so small—the solubility expression is, for the solubility in water quoted above,

$$\log [Cu^{++}][IO_3^-]^3 - 3F(I) = \bar{8}{\cdot}8790$$

where

$$F(I) = \log [I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) - 0{\cdot}2I]$$

I is the ionic strength, and the activity expression is that proposed by Davies (*J.*, 1938, 2093). Where the solubility in water differed from this, the above expression was accordingly modified. From the solubility product expression and a preliminary I value, a first value of Cu^{++} is obtained. Then from the relations

$$[CuR^+] = \text{Solubility} - [Cu^{++}] - [Cu(IO_3)^+]$$

and

$$[R^-] = 2[Cu^{++}] + [Cu(IO_3)^+] + [Na^+] + [H^+] - [IO_3^-]$$

where R^- refers to the organic anion, the concentrations of R^- and CuR^+ are obtained. The true figures were derived by approximation until they became constant. Allowance was made for sodium iodate formation (Macdougall and Davies, *J.*, 1935, 1416). The dissociation constants were calculated from

$$\log K = \log [Cu^{++}][R^-]/[CuR^+] - 2F(I)$$

The essential data are recorded in Table I where the concentrations are given in mmols. or mg.-ions per l., and the solubility in the salt solutions is listed in the column marked *S*. The first column contains the concentrations of acid HR, and the second column contains the sodium hydroxide concentrations used in making the solvent solutions. Because the solubility of cupric *n*-hexanoate proved to be rather small, only dilute solutions of the solvent mixture were used in this case.

TABLE I.

Solubility Data (*concentrations* × 10^3).

HR.	NaOH.	$S(H_2O)$.	S.	pH.	$[Cu^{++}]$.	$[CuR^+]$.	$[R^-]$.	10^3I.	10^3K.	
(1) R^- = *Formate.*										
30·40	12·37	3·33	4·16	3·7	2·63	1·45	10·14	21·49	10·4	
34·62	24·42	—	4·84	4·0	2·32	2·44	22·10	33·97	10·6	Mean **10·5**
43·43	31·65	—	5·21	4·1	2·24	2·90	28·86	41·38	10·6	
(2) R^- = *Acetate.*										
18·63	11·19	3·33	4·42	4·5	2·28	2·06	9·16	20·20	5·8	
138·2	32·56	—	5·89	4·0	1·71	4·11	28·55	41·90	5·6	Mean **5·7**
153·3	44·52	—	6·54	4·2	1·56	4·92	39·68	54·13	5·6	
(3) R^- = *Propionate.*										
27·00	13·63	3·33	4·61	4·8	2·18	2·35	11·30	22·59	5·9	
83·85	27·27	—	5·52	4·5	1·84	3·61	24·12	36·64	6·1	Mean **6·0**
128·8	29·98	—	5·71	4·2	1·79	3·85	26·31	39·37	5·9	
(4) R^- = n-*Butyrate.*										
76·60	19·90	3·36	4·92	4·6	2·15	2·70	17·23	29·10	7·2	
153·2	39·80	—	5·96	4·6	1·85	4·04	35·79	49·40	7·4	Mean **7·3**
191·0	49·74	—	6·38	4·4	1·71	4·61	45·18	59·45	7·2	
(5) R^- = iso*Butyrate.*										
31·33	11·13	3·33	4·36	4·4	2·34	1·94	9·24	20·20	6·4	
62·66	18·99	—	4·86	4·3	2·12	2·67	16·36	28·10	6·9	Mean **6·7**
93·99	28·90	—	5·48	4·3	1·90	3·51	25·45	38·17	6·7	
(6) R^- = n-*Valerate.*										
61·60	16·72	3·33	4·65	4·0	2·25	2·32	14·52	25·96	7·6	
53·80	22·73	—	5·02	4·6	2·10	2·85	19·93	31·95	7·5	Mean **7·5**
123·2	33·44	—	5·60	4·5	1·91	3·62	29·86	42·82	7·5	
(7) R^- = iso*Valerate.*										
34·68	11·98	3·33	4·27	4·3	2·49	1·70	10·34	21·26	8·6	
46·88	15·99	—	4·56	4·4	2·33	2·15	13·89	25·22	8·2	Mean **8·3**
93·76	29·86	—	5·32	4·4	2·04	3·21	26·70	39·26	8·2	
(8) R^- = *Trimethylacetate.*										
48·02	10·06	3·33	4·25	4·3	2·42	1·75	8·37	19·19	6·7	
96·03	20·12	—	4·98	4·3	2·06	2·84	17·34	29·23	6·6	Mean **6·5**
123·0	25·80	—	5·36	4·3	1·91	3·40	22·50	35·00	6·3	
(9) R^- = n-*Hexanoate.*										
35·0	7·95	3·33	3·98	4·5	2·67	1·23	6·75	17·28	8·7	Mean **9·0**
40·0	10·33	—	4·13	4·1	2·59	1·46	8·96	19·71	9·2	
(10) R^- = *Chloroacetate.*										
39·77	37·67	3·36	4·75	4·0	2·88	1·79	35·98	48·20	26·4	
70·08	67·11	—	5·51	4·0	2·64	2·79	64·42	77·85	24·0	Mean **24·5**
88·72	87·28	—	6·04	4·0	2·53	3·44	83·94	98·28	22·5	

TABLE I—*continued.*

HR.	NaOH.	$S(H_2O)$.	S.	pH.	$[Cu^{++}]$.	$[CuR^+]$.	$[R^-]$.	10^3I.	10^3K.	
(11) R^- = *Bromoacetate.*										
54·75	52·01	3·36	5·07	4·5	2·87	2·12	49·93	62·75	28·5	Mean 25·5
69·58	66·92	—	5·53	4·1	2·68	2·77	64·25	77·76	24·5	
89·74	87·28	—	5·99	4·6	2·57	3·35	83·96	98·23	23·5	
(12) R^- = *Phenylacetate.*										
23·50	10·39	3·33	4·07	4·2	2·68	1·30	9·17	19·88	10·8	Mean 10·6
29·37	12·90	—	4·23	4·1	2·58	1·57	11·42	22·36	10·5	
44·06	19·48	—	4·60	4·2	2·41	2·11	17·45	28·94	10·5	
(13) R^- = *Glycollate.*										
13·67	13·11	3·33	5·96	4·4	1·27	4·63	8·53	21·62	1·3	Mean 1·2
18·23	17·19	—	6·65	4·6	1·12	5·48	11·74	26·05	1·3	
22·78	22·16	—	7·55	4·6	0·92	6·58	15·61	31·50	1·1	
(14) R^- = *Lactate.*										
7·17	6·24	3·34	4·75	4·4	1·77	2·91	3·38	14·56	1·3	Mean 1·2
10·90	9·49	—	5·42	4·3	1·44	3·92	5·64	17·76	1·2	
14·33	13·56	—	6·36	5·0	1·14	5·16	8·41	22·17	1·0	
(15) R^- = *Trichlorolactate.*										
13·58	12·66	3·33	3·94	3·7	3·01	0·84	12·05	22·83	24·1	Mean 25·2
27·16	25·77	—	4·42	3·9	2·86	1·48	24·44	36·01	23·4	
29·27	29·54	—	4·45	4·2	2·95	1·42	28·12	39·83	28·1	
(16) R^- = *a-Bromobutyrate.*										
20·06	18·94	3·34	4·07	3·9	3·14	0·84	18·25	29·30	36·0	Mean 35·0
25·64	23·73	—	4·22	3·7	3·09	1·04	22·91	34·31	34·0	
(17) R^- = *β-Iodopropionate.*										
53·20	29·88	3·33	4·95	4·2	2·37	2·50	27·46	39·58	12·3	Mean 12·2
63·85	37·37	—	5·27	4·1	2·26	2·93	34·55	47·19	12·2	
85·12	47·82	—	5·66	4·2	2·15	3·44	44·46	57·74	12·0	

DISCUSSION.

In the figure comparative plots are drawn of the dissociation constants of the acids, the copper salts, and a few figures which are available for some other cations. The general parallel nature of these is striking evidence that the same influences operate in governing the dissociation constants of both acids and salts. The main exception to this is where the anion contains a hydroxyl group, when the metallic cations become bound by chelation forces. This has been illustrated previously with calcium (Davies, *J.*, 1938, 277). With the exception of the hydroxy-acids, the general trends in the dissociation constants of the acids and salts may be interpreted in terms of the electron-displacement abilities of the various substituents; these effects have been interpreted in detail by Ingold and others (*e.g.*, *Chem. Reviews*, 1934, **15**, 225) under the general title of inductive effect. The influence of substituents on the dissociation constants of the acids is related to their electron-attracting capacities which, for the examples with which we wish to draw comparison, are in the order Halogens > OH > H > alkyl (Dippy, *Chem. Reviews*, 1939, **25**, 351), *i.e.*, this is the order of decreasing values of the dissociation constants. Comparison of the data for the acids with those of the copper salts (Table II) shows that this order is maintained by the latter except when, with a hydroxyl group, chelation forces are operative.

With the series formate to hexanoate, the order of the dissociation constants of the acids and of the salts is not identical. Thus the values of the normal acids tend to become smaller as the alkyl group increases in length although *n*-butyric acid shows marked departure from this generalisation, having a larger value than its neighbours. With these acids, therefore, the electron-repulsion capacity of the alkyl group tends to increase as the chain length grows. The copper salts of the normal acids, on the other hand, although showing an analogous decrease in their dissociation constants on passage from formate to acetate, thereafter show a steady rise.

The apparent anomaly in the dissociation constant of *n*-butyric acid is considered by Jenkins and Dippy (*J. Amer. Chem. Soc.*, 1940, **62**, 483) to be mainly related to C–CH_3 and C–O dipole interaction resulting from restricted rotation favouring a "*cis*"-configuration; Dippy (*loc. cit.*) suggests that the acids beyond *n*-butyric acid are also involved, to some extent, in a similar chelation process. It therefore appears that this factor which tends to discourage the combin-

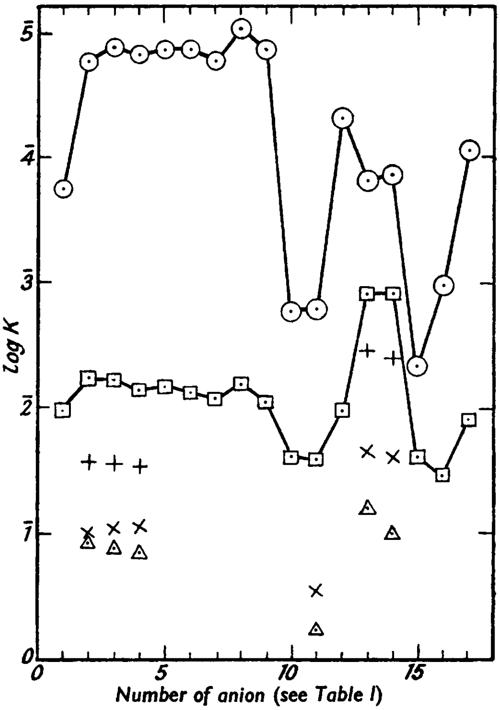
TABLE II.

Dissociation constants of acids and copper salts.

	Acid, × 10^5.	Copper salt, × 10^3.		Acid, × 10^5.	Copper salt, × 10^3.
Formate	17·1[a]	10·5	Chloroacetate ...	138[a]	24·5
Acetate	1·75[a]	5·7	Bromoacetate ...	138[b]	25·5
Propionate	1·34[a]	6·0	Phenylacetate ...	4·88[a]	10·6
n-Butyrate	1·51[a]	7·3	Glycollate.........	14·8[c]	1·2
*iso*Butyrate	1·38[a]	6·7	Lactate	13·7[d]	1·2
n-Valerate.........	1·38[a]	7·5	Trichlorolactate	460[b]	25·2
*iso*Valerate	1·67[a]	8·3	α-Bromobutyrate	106[b]	35·0
Trimethylacetate	0·89[a]	6·5	β-Iodopropionate	9[b]	12·2

[a] Dippy, *loc. cit.* [b] Landolt-Bornstein's " Tabellen," Main vol., p. 1123. [c] Nims, *J. Amer. Chem. Soc.*, 1936, **58**, 987. [d] Nims and Smith, *J. Biol. Chem.*, 1936, **113**, 145.

ation of the anions with H^+ ions shows up more markedly when Cu^{++} ions are substituted for the latter. To some extent the especially noticeable effect in the case of *n*-butyric acid, which has a larger dissociation constant than *n*-valeric acid, is reflected by the values for the copper salts, since the *n*-butyrate constant is nearly as large as that of the *n*-valerate.



⊙, *Acids; Landolt-Bornstein's " Tabellen," Main vol., p.* 1123; *Dippy,* loc. cit. ⊡, *Copper;* +, *Zinc;* ×, *Calcium;* △, *Barium; Cannan and Kibrick,* loc. cit. (*corrected for ionic strengths*); *Davies and Wyatt,* Trans. Faraday Soc., 1949, **45**, 770.

With the substitution of methyl groups at the α-carbon atom, as exemplified by the acids acetic, propionic, *iso*butyric, and trimethylacetic acids, the electron-repulsion forces tend to be accumulative so that there is a fall in the dissociation constants. With the copper salts this effect is not so marked although the trimethylacetate certainly shows stronger association than the *iso*butyrate, and the dissociation constants of both of these are smaller than those of the corresponding normal salts. That there are not exact similarities between the acids and the copper salts is undoubtedly due to the larger size and different charge of the Cu^{++} ion.

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