

**836.** *Dissociation Constants of the Alkaline-earth Salts of Some Monocarboxylic Acids.*

By C. A. COLMAN-PORTER and C. B. MONK.

The dissociation constants of a number of organic salts of calcium, strontium, and barium have been obtained from the solubilities of the iodates in solutions of the sodium salts of the acids. The results are discussed in terms of inductive effects, ion sizes, and ionisation potentials. Chelation occurs when the anion contains an OH or NH<sub>2</sub> group.

In a previous paper (Lloyd, Wycherley, and Monk, *J.*, 1951, 1786) the dissociation constants of some cupric salts of organic acids were reported and the values compared with those of the corresponding acids. Inductive effects, which can largely account for the variations in the constants of the acids (Dippy, *Chem. Reviews*, 1939, **25**, 351), can also explain some of the trends in the cupric series. There are marked differences, however, since the cupric salts of hydroxy-acids show chelation, and the inductive effects appear to be modified by the size and charge of the cupric ion.

Owing to the lack of sufficient data for other salts it is not clear what influences can be attributed to the nature of the cation and we have therefore extended our studies to the

alkaline-earth series in the hope that these cations, whose properties vary systematically, will reveal further information. The solubility method used previously for the cupric salts (*loc. cit.*) was adopted. This method, which depends on the solubility of the iodate in solutions of the sodium salts of the acids, was first used by Davies (*J.*, 1938, 277) to study the ionisation of some calcium salts of organic acids. Apart from these results, and those of Cannan and Kibrick (*J. Amer. Chem. Soc.*, 1938, 60, 2314) which are based on pH measurements, no systematic studies of the particular salts considered here have been published, although some isolated figures (to which reference is made later) are available.

## EXPERIMENTAL

Calcium iodate was prepared by the method of Wise and Davies (*J.*, 1938, 273), barium iodate by that of Davies and Wyatt (*Trans. Faraday Soc.*, 1949, 45, 770), and strontium iodate by that of Colman-Porter and Monk (*J.*, 1952, 1312). The solubility determinations were made as described previously (*idem, ibid.*). Solutions of the sodium salts were prepared by addition of carbonate-free "AnalaR" sodium hydroxide to solutions of the acids until the pH was about 7. The formic and acetic acids were "AnalaR," Kahlbaum's lactic acid was used, and the other acids were of laboratory grade except *isobutyric* acid, which was a triple-distilled sample, and the glycollic acid. This was prepared by hydrolysis of "AnalaR" chloroacetic

TABLE 1.

	Soly. in water ( $10^3M$ )	$10^3\{S.P.\}$	$K_{MIO_3^+}$	$K_{MOH^+}$
Calcium .....	7.84	71.19	0.13 <sup>a</sup>	0.05 <sup>b</sup>
Strontium .....	5.87	32.89	0.10 <sup>c</sup>	0.11 <sup>c</sup>
Barium .....	0.809	0.1480	0.08 <sup>d</sup>	—

<sup>a</sup> Wise and Davies, *loc. cit.* <sup>b</sup> Davies and Hoyle, *J.*, 1951, 233. <sup>c</sup> Colman-Porter and Monk, *loc. cit.* <sup>d</sup> MacDougall and Davies, *loc. cit.*

TABLE 2. Solubility data obtained by using calcium iodate (concn.  $\times 10^3$ ).

[NaR]	Soly.	[CaR <sup>+</sup> ]	$10^3I$	$K$	[NaR]	Soly.	[CaR <sup>+</sup> ]	$10^3I$	$K$
		Formate					<i>n</i> -Valerate		
51.10	9.67	0.96	77.1	0.17	33.69	9.03	0.22	59.3	0.54
61.00	9.96	1.24	87.2	0.15	43.24	9.28	0.31	69.3	0.48
75.00	10.25	1.35	101.8	0.17	53.34	9.52	0.38	80.0	0.47
		Acetate					<i>iso</i> Valerate		
37.27	9.27	0.71	62.6	0.18	32.82	9.15	0.20	64.8	0.68
51.00	9.68	0.99	76.9	0.16	55.96	9.55	0.30	82.8	0.63
72.13	10.21	1.39	98.8	0.16	62.46	9.69	0.36	89.6	0.57
		Propionate					Trimethylacetate		
46.71	9.47	0.66	72.7	0.23	28.52	8.93	0.32	53.6	0.32
59.88	9.83	0.93	86.3	0.20	43.28	9.36	0.54	69.2	0.27
75.00	10.19	1.18	102.0	0.19	62.69	9.83	0.77	89.5	0.26
		<i>n</i> -Butyrate					Bromoacetate		
57.73	9.70	0.66	84.3	0.28	50.03	9.47	0.43	76.5	0.39
68.22	9.91	0.71	95.3	0.31	60.00	9.71	0.56	86.8	0.35
78.72	10.16	0.90	106.2	0.27	72.99	9.95	0.56	100.5	0.42
		<i>iso</i> Butyrate					Glycine salt *		
32.63	9.04	0.36	58.0	0.32	35.40	9.74	2.05	59.2	0.046
43.99	9.35	0.48	70.0	0.31	51.43	10.41	2.92	75.6	0.045
74.32	10.05	0.80	101.6	0.29	66.34	10.98	3.59	90.8	0.044

\* The glycine solutions were made from equal concentrations of HR and NaOH. They were corrected for hydrolysis: pH = 11.3, 11.0, 11.0:  $[OH^-] = 2.48, 1.25, 1.29 (\times 10^3)$ ;  $[Ca(OH)^+] = 0.15, 0.07, 0.07 (\times 10^3)$ , respectively.

acid with marble chips; the resulting calcium glycollate was recrystallised from water until it was chloride-free, and then converted into the acid by a column of the ion-exchange resin Amberlite I.R.-100.

The calculations were made as in previous cases (Davies, 1938, *loc. cit.*; Lloyd, Wycherley, and Monk, *loc. cit.*). Representing the cations by  $M^{2+}$  and the organic anions by  $R^-$ , we have

$$\log [M^{2+}][IO_3^-]^2 - 3F(I) = \log \{S.P.\}$$

where {S.P.} represents the solubility product and

$$F(I) = \log \{I^{\frac{1}{2}} / (1 + I^{\frac{1}{2}}) - 0.2I\} \quad (\text{Davies, } J., 1938, 2093)$$

$$[MR^+] = \text{Solubility} - [M^{2+}] - [MIO_3^+]$$

$$[R^-] = 2[M^{2+}] + [MIO_3^{3+}] + [Na^+] + [MR^+] - [IO_3^-]$$

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

Allowance was made for undissociated sodium iodate (MacDougall and Davies, *J.*, 1935, 1416), for which  $K = 3.0$  and for the ion-pairs formed between  $M^{2+}$  and  $IO_3^-$  (the dissociation constants of these are given in Table 1). Since the glycine and alanine solutions were alkaline, pH measurements of these were made to correct for  $OH^-$  and  $M(OH)^+$  ions. Table 1 contains the dissociation constants of the latter, together with the solubilities of the iodates in water at  $25^\circ \pm 0.03^\circ$ . The concentrations and results of the calculations are summarised in Tables 2—4.

TABLE 3. *Solubility data obtained by using strontium iodate (concns.  $\times 10^3$ ).*

[NaR]	Soly.	[SrR <sup>+</sup> ]	10 <sup>3</sup> I	K	[NaR]	Soly.	[SrR <sup>+</sup> ]	10 <sup>3</sup> I	K
		Formate					Bromoacetate		
44.55	7.21	0.56	64.2	0.21	50.03	7.20	0.25	70.3	0.53
66.82	7.61	0.68	87.4	0.24	60.00	7.37	0.30	80.6	0.52
75.47	7.78	0.83	96.2	0.22	72.99	7.58	0.34	94.1	0.54
		Acetate					Glycollate		
33.75	6.90	0.26	53.1	0.36	46.68	7.71	1.87	65.2	0.055
50.93	7.26	0.38	71.1	0.35	56.95	8.10	2.42	75.5	0.048
67.50	7.55	0.47	88.3	0.36	75.00	8.50	2.75	94.1	0.053
		Propionate					Lactate		
52.63	7.24	0.23	73.0	0.61	19.96	6.66	0.50	38.2	0.110
70.41	7.54	0.32	91.4	0.56	39.92	7.27	0.97	59.5	0.105
77.84	7.65	0.34	99.2	0.58	59.88	7.72	1.24	79.6	0.112
		<i>n</i> -Butyrate					Glycine salt *		
50.10	7.19	0.19	70.4	0.71	39.00	7.20	0.82	58.1	0.119
61.48	7.38	0.24	82.2	0.67	47.04	7.37	0.88	66.5	0.128
77.39	7.61	0.27	98.6	0.73	70.64	7.89	1.28	90.8	0.123
		<i>n</i> -Valerate					Alanine salt *		
57.82	7.28	0.10	78.5	1.5	40.12	7.13	0.57	59.5	0.180
70.40	7.48	0.13	91.7	1.4	58.76	7.52	0.76	78.9	0.187
		Trimethylacetate							
48.59	7.15	0.17	68.8	0.70	70.92	7.75	0.89	91.4	0.186
62.79	7.40	0.23	83.6	0.71					
73.94	7.57	0.35	95.2	0.75					

\* The glycine and alanine solutions were made from equal concentrations of acid and sodium hydroxide. They were corrected for hydrolysis: (a) Glycine: pH = 10.6, 11.1, 11.1;  $[OH^-] = 0.60, 1.60, 1.60 (\times 10^3)$ ;  $[Sr(OH)^+] = 0.02, 0.04, 0.03 (\times 10^3)$ , respectively. (b) Alanine: pH = 10.8, 10.9, 11.0;  $[OH^-] = 0.80, 1.00, 1.30 (\times 10^3)$ ;  $[Sr(OH)^+] = 0.02, 0.02, 0.03 (\times 10^3)$ , respectively.

TABLE 4. *Solubility data obtained by using barium iodate (concns.  $\times 10^3$ ).*

[NaR]	Soly.	[BaR <sup>+</sup> ]	10 <sup>3</sup> I	K	[NaR]	Soly.	[BaR <sup>+</sup> ]	10 <sup>3</sup> I	K
		Formate					<i>n</i> -Valerate		
51.10	1.130	0.088	54.3	0.26	57.82	1.125	0.015	61.1	1.8
61.00	1.171	0.115	64.2	0.23	70.40	1.162	0.022	73.8	1.4
75.00	1.213	0.128	78.3	0.25					
		Acetate					Trimethylacetate		
37.27	1.070	0.051	40.3	0.35	62.79	1.146	0.035	66.1	0.82
51.00	1.120	0.054	54.2	0.44	70.40	1.177	0.038	77.4	0.86
72.13	1.191	0.082	75.5	0.38					
		Propionate					Glycollate		
59.88	1.141	0.038	63.2	0.72	36.45	1.112	0.179	39.4	0.090
74.94	1.182	0.045	78.3	0.73	56.95	1.209	0.251	60.0	0.092
88.30	1.217	0.054	91.7	0.70					
		<i>n</i> -Butyrate					Lactate		
52.30	1.111	0.024	55.5	1.0	19.96	0.997	0.065	22.8	0.15
59.59	1.135	0.028	62.9	1.0	39.92	1.096	0.096	43.0	0.19
77.39	1.184	0.034	80.8	1.0	59.88	1.184	0.162	63.1	0.16

## DISCUSSION

The average dissociation constants, together with those collected from other sources, are given in Table 5. The values for magnesium acetate, propionate, butyrate, lactate, and glycollate were calculated from Cannan and Kibrick's data (*loc. cit.*). The original figures are not comparable with ours since they are based on measurements made at an ionic strength of 0.2 by an E.M.F. method of a somewhat empirical nature. The differences between the pK data of their calcium and magnesium results were used to estimate the values for magnesium salts given in Table 5 from our calcium results.

TABLE 5.—Average dissociation constants at 25°.

Anion	Mg	Ca	Sr	Ba	Limiting anion mobility
(1) Formate .....	—	0.16	0.22	0.25	54.6 <sup>g</sup>
(2) Acetate .....	0.165 <sup>a</sup>	0.17	0.36	0.39	40.9 <sup>g</sup>
(3) Propionate .....	0.19 <sup>a</sup>	0.21	0.58	0.71	35.8 <sup>g</sup>
(4) <i>n</i> -Butyrate .....	0.275 <sup>a</sup>	0.29	0.70	1.0	35.1 <sup>h</sup>
(5) <i>iso</i> Butyrate .....	—	0.31	—	—	34.2 <sup>h</sup>
(6) <i>n</i> -Valerate .....	—	0.50	1.5	1.6	33.4 <sup>h</sup>
(7) <i>iso</i> Valerate .....	—	0.63	—	—	32.7 <sup>h</sup>
(8) Trimethylacetate .....	—	0.28	0.72	0.84	31.9 <sup>h</sup>
(9) Bromoacetate .....	—	0.39	0.53	0.57 <sup>e</sup>	39.3 <sup>i</sup>
(10) Lactate .....	0.047 <sup>a</sup>	0.034 <sup>e</sup>	0.109	0.17	—
(11) Glycollate .....	0.039 <sup>a</sup>	0.026 <sup>e</sup>	0.049	0.091	—
(12) Glycine salt .....	0.0085 <sup>b</sup>	0.045	0.123	0.17 <sup>f</sup>	—
(13) Alanine salt .....	0.016 <sup>b</sup>	0.058 <sup>d</sup>	0.184	0.17 <sup>f</sup>	—

<sup>a</sup> Cannan and Kibrick (corrected). <sup>b</sup> Monk, *Trans. Faraday Soc.*, 1951, **47**, 297. <sup>c</sup> Davies, *loc. cit.* <sup>d</sup> Davies and Waind, *J.*, 1950, 301. <sup>e</sup> Davies and Wyatt, *loc. cit.* <sup>f</sup> Monk, *Trans. Faraday Soc.*, 1951, **47**, 1233. <sup>g</sup> Harned and Owen, "Physical Chemistry of Electrolytic Solutions," Reinhold, 1943, p. 172. <sup>h</sup> Dippy, *J.*, 1938, 1222. <sup>i</sup> I.C.T., VI, 262.

There are very few published data with which comparisons can be made. Davies and Wyatt (*loc. cit.*) cite a lower figure of 0.28 for calcium bromoacetate, but this was based on a personal communication and it is not possible to account for the difference. Bell and Waind (*J.*, 1951, 2357) suggest that calcium acetate has a  $K$  of  $>2$  on the basis of kinetic studies. This and other values given by these authors are higher than those obtained by other methods and they have intimated that the kinetic values may be subject to error. Two series of results have been published for the calcium glycine salt. Davies (*loc. cit.*) quotes 0.045 and 0.038 from two measurements, and Davies and Waind (*loc. cit.*) obtained 0.037. Our measurements clearly support Davies's higher value. Joseph (*J. Biol. Chem.*, 1946, **164**, 529) studied a number of organic salts by an E.M.F. method, but calculated the apparent dissociation constants at an ionic strength of 0.15. Applying an approximate correction for this, we have  $K = 0.10$  for calcium acetate and 0.048 for calcium lactate. These are of the same order as the results given in Table 5, but differ numerically.

The dissociation constants of the salts of organic acids are undoubtedly related to the characteristics both of the cations and of the organic anions. First, it is apparent that our  $K$  values are in the order Ba  $>$  Sr  $>$  Ca  $>$  Mg. The lactate and glycollate of magnesium are possible exceptions but, for the reasons mentioned earlier, they may not be the true values. The general order is in the reverse direction to that found when these cations associate with low-valency inorganic anions, for which it has been suggested that hydrated ions form the ion pairs (Jones, Monk, and Davies, *J.*, 1949, 2693; Denney and Monk, *Trans. Faraday Soc.*, 1951, **47**, 992). A first suggestion with the organic series is therefore that association may involve unhydrated cations, since the crystallographic radii of the alkaline-earth cations (Table 6) have the same trend as the dissociation constants of the organic salts. This cannot be completely true, however, since the differences in the  $K$  values are not so marked as are the differences between the cation radii and furthermore would not account for the much smaller values of the cupric salts (*loc. cit.*). One possibility to account for the stability of metallic complexes formed with chelating agents such as aldehydes and amines is that their stabilities may be related to the ionisation potentials of the metals (Irving and Williams, *Nature*, 1948, **162**, 746; Calvin and Melchior, *J. Amer. Chem. Soc.*, 1948, **70**, 3270). This has so far only been applied to the transition metals and

where chelation occurs. We have applied this concept to our own data in a few cases, and Fig. 1 shows a plot of some  $pK$  values against the second ionisation potentials of the alkaline-earth metals and copper (Table 6; data of Ahrens, *Nature*, 1952, 169, 463; Rice,

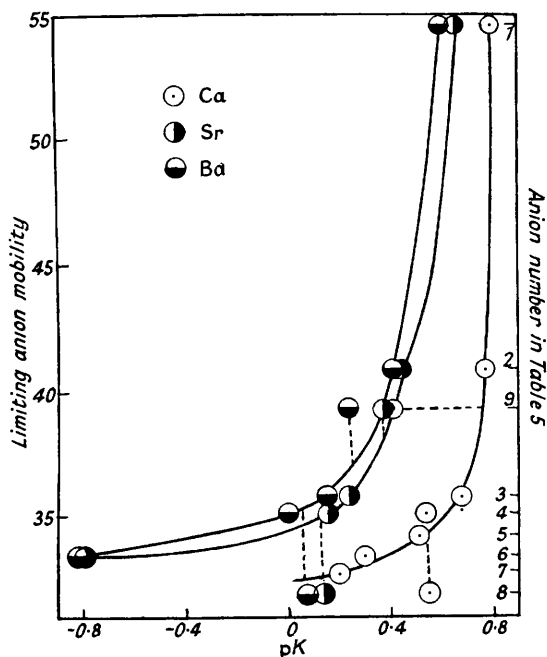
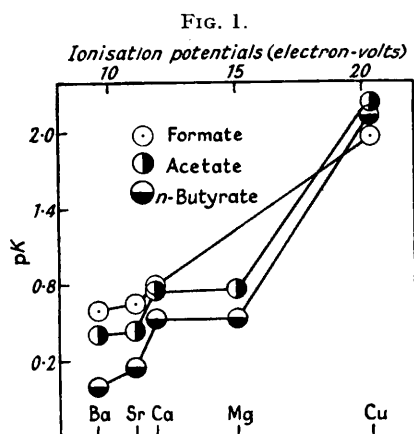
TABLE 6.

	Mg	Ca	Sr	Ba	Cu
Second ionisation potentials (ev) .....	15.03	11.82	10.98	9.95	20.3
Ionic radii (Å) .....	0.66	1.18	1.32	1.53	0.72

“Electronic Structure and Chemical Binding,” McGraw-Hill, New York, 1940, pp. 98, 220). The results do not cover enough metals for a thorough discussion, but the plots do indicate that there is a rough relation. Similar plots are obtained with the other anions.

With these organic anions, the electrical centre is located at the carboxyl group, and is subject to a certain amount of displacement which is due partly to interionic forces and

FIG. 2.



partly to the inductive effects of the various groups attached to the carboxyl group. Such displacements probably do not occur to any marked extent with inorganic anions owing to their electrical symmetry. The effects of electron-displacing groups on the dissociation constants of acids (Dippy, *loc. cit.*) were found to be considerably modified on replacing hydrogen by cupric ions (*loc. cit.*), and it is apparent that with the alkaline-earth cations inductive effects have little influence on the extent of ionisation. The main effects of the anions appear to depend on their relative sizes, which are no doubt related to the influence of the attached groups on the mean statistical distances of closest approach of the electrical centres of the associating ions. Plots illustrating this point are shown in Fig. 2, where the  $pK$  data are plotted against the limiting anion mobilities (Table 5). The latter, from Stokes's law, are related to the mean anion radii. The only cases where inductive effects appear to modify the effective anion size are the trimethylacetates and bromoacetates.

Where hydroxyl and amino-groups are present, the dissociation constants of the salts are much smaller. It has been previously remarked in conjunction with calcium salts (Davies, *loc. cit.*) that this can be attributed to chelation; the cupric salts (*loc. cit.*) and the present data conform to this view. Introduction of a methyl group markedly decreases the dissociation constants of the salts of these two types of acid. Although these differences may be due to the increase in the mean anion radius, yet this increase may not be sufficient

to account for all of the marked changes on passing from glycollate to lactate, and from the glycine to the alanine salt. Thus the limiting anion mobilities of the former pair are 40·8 and 35·5 respectively (unpublished work), indicating a radius ratio of 1 : 1·15, while the dissociation constant ratios vary from 1·3 to 2·0. It would appear that the methyl group modifies the binding capacity of the chelating group.

It seems then, from the available evidence, that the dissociation constants of the mono-carboxylate salts become smaller (*a*) with metals of higher ionisation potentials and (*b*) if chelating groups are present in the anion, and increase as the anion size increases. Induction effects, which are short-range forces, become of less importance with metals of low ionisation potential. There are still, however, the effects of cation size and ion-solvation to consider, but until other metals, especially magnesium (which is the most hydrated alkaline-earth cation) have been investigated, these aspects remain obscure.

THE EDWARD DAVIES CHEMICAL LABORATORIES,  
UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH.

[Received, May 30th, 1952.]

---