339. *Chemical Constitution and the Dissociation Constants of Mono-carboxylic Acids. Part XIX.* Dihydroxy- and Dichloro-benzoic Acids.*

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The strengths of all six dihydroxybenzoic acids and three dichlorobenzoic acids in water have been determined conductometrically. The qualitative effect of introducing a second substituent into the monosubstituted benzoic acid is consistent with expectation although in certain cases substantial departures from additivity have been observed.

THE strengths of all six dihydroxybenzoic acids in water (Table 1) have now been determined by a standard procedure, and the effect of introducing a second hydroxyl group into the monohydroxybenzoic acid system is qualitatively that to be expected from a knowledge of the polar character $(-I+M)$ of the hydroxyl substituent (10^5K for *o*-, *m*-, and *p*-hydroxybenzoic acids = 101, 3·27, and 2·94, respectively). Thus in both the salicylic acid and the *m*-hydroxybenzoic acid system, the introduction of a *meta*-hydroxyl group has the effect of strengthening the acid, whereas the entry of *para*-hydroxyl depresses the strength. Quantitative examination of the K data reveals, however, that only in the

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case of 2,4-dihydroxybenzoic acid is there absolute additivity.[1-3] This is doubtless connected with the fact that there is no possibility of steric or mesomeric interaction here between the two hydroxyl groups, whereas both of these additional factors might operate in 2,3- or 3,4-dihydroxybenzoic acids so as to modify their strengths. It is significant, therefore, that departures of —2·9% and —38% from additivity are observed with these

TABLE 1. *Dissociation constants* ($10^3 K$).

Benzoic acid	This paper	Earlier values	M. p.	Benzoic acid	This paper	Earlier values	M. p.
2,3-Dihydroxy-	1·22	1·14[a]	206—207°	2,6-Dihydroxy-	89	50[a]	172° (decomp.)
2,4-Dihydroxy-	0·473	0·496[b]	226 (decomp.)	3,4-Dihydroxy-	0·0323	0·033[a]	203
		0·515[a,c]		3,5-Dihydroxy-	0·0915	0·091[a]	237—238
2,5-Dihydroxy-	1·12	1·08[a]	201—202	2,4-Dichloro- ...	2·09		160—161
		1·10[b]		2,5-Dichloro- ...	3·42		154
		1·18[d]		2,6-Dichloro- ...	25·5		144
		1·30[e]					

[a] Ostwald, *Z. phys. Chem.*, 1889, **3**, 248.
[b] Suss, *Monatsh.*, 1905, **26**, 1331.
[c] Kendall, *Chem. Zentr.*, 1914, **1**, 842.
[d] Boeschen, *Rec. Trav. chim.*, 1921, **40**, 576.
[e] Wightman and Jones, *J. Amer. Chem. Soc.*, 1924, **46**, 94.

acids; the observed departure for the 2,5-acid (where the additional mesomeric factor alone operates) is —5·5%. The remarkably high strength of 2,6-dihydroxybenzoic acid, already well-known, has received confirmation; an explanation of this feature has already been advanced.[4]

A wholly unexpected result is the strength of 3,5-dihydroxybenzoic acid which is very little greater than that of *m*-hydroxybenzoic acid and shows a departure of —32% from additivity. It is not possible to envisage any mutual interaction between the two hydroxyl groups in this structure, and the phenomenon cannot yet be explained.

The dissociation constants of three dichlorobenzoic acids have also been determined. The introduction of a second chlorine substituent into *o*-chlorobenzoic acid leads, as expected, to a substantial enhancement of strength, by virtue of the —I effect, although the effect from the *para*-position (where +M operates) is less than from the *meta*-position as the data in Table 1 reveal (cf. $10^3 K$ for *o*-, *m*-, and *p*-chlorobenzoic acids = 1·14, 0·148, and 0·105, respectively). In 2,6-dichlorobenzoic acid the very large increment in strength is doubtless due to the additional steric factor introduced by the second substituent. Quantitative consideration of the data shows that entry of the second chlorine substituent produces a small departure (*ca.* +3 to +6%) from additivity in each of the three acids.

Specimens of the remaining acids of this series proved so sparingly soluble in water that even very approximate measurements of their dissociation could not be made.

These data, coupled with those published recently by us,[2,3] go some way to making good the deficiency of reliable dissociation-constant data for disubstituted aromatic acids.

EXPERIMENTAL

Materials.—2,6-Dichlorobenzoic acid was prepared from 2,6-dichlorotoluene by side-chain bromination, followed by oxidation with alkaline potassium permanganate as described by Norris and Bearse.[5] The remaining acids were purchased.

All acids were recrystallised from conductivity water or from aqueous acetone, except 2,5-dihydroxybenzoic acid which was recrystallised from benzene–acetone. Final specimens were dried in individual vacuum desiccators over silica gel for at least 3 weeks, and the equivalents were confirmed by alkalimetry.

[1] Shorter and Stubbs, *J.*, 1949, 1180.
[2] Dippy, Hughes, and Laxton, *J.*, 1956, 2995.
[3] Bray, Dippy, Hughes, and Laxton, *J.*, 1957, 2405.
[4] Baker, *Nature*, 1936, **137**, 236.
[5] Norris and Bearse, *J. Amer. Chem. Soc.*, 1940, **62**, 956.

Conductivity Measurements.—The procedure and equipment used have already been described,[6] and the values of K were derived by the usual method. Λ_0 was the self-consistent value obtained by Ives's extrapolation method,[7,8] and no additional significance is attached to

TABLE 2.

Left column:

10^3C	Λ	10^3K
2,3-Dihydrobenzoic acid		
1·212	230·9	1·22
0·8441	252·4	1·21
0·5933	272·8	1·21
0·5304	278·7	$1·20_5$
0·5208	280·6	$1·22_5$
0·4528	288·0	$1·22_5$
0·3866	296·4	1·24
0·3802	296·1	$1·21_5$
0·2004	322·8	1·20
	$\Lambda_0 = 370·4$	
2,6-Dihydroxybenzoic acid		
2·144	370·5	150 *
1·277	376·4	106
1·185	375·6	81·9
0·8367	378·6	107
0·8301	378·4	97·8
0·5187	379·8	77·0
0·5099	380·0	80·9
0·4141	380·2	63·5
0·2974	381·2	102·3
0·3514	380·9	66·3
0·2761	382·2	107·9
	$\Lambda_0 = 385·6$	
2,4-Dichlorobenzoic acid		
0·5170	307·2	2·08
0·4902	309·6	2·08
0·4594	313·3	$2·12_5$
0·4413	313·2	$2·04_5$
0·3741	320·8	$2·10_5$
0·3394	324·8	$2·13_5$
0·3285	325·5	$2·10_5$
0·2247	337·1	2·10
0·2200	336·2	1·99
0·1580	346·0	2·14
	$\Lambda_0 = 371·0$	

10^3C	Λ	10^3K
2,4-Dihydroxybenzoic acid		
5·127	102·5	0·47
2·701	133·3	0·47
2·436	138·3	0·47
1·851	153·9	0·47
1·326	173·6	0·47
1·138	183·0	0·47
1·093	185·5	0·47
0·8056	204·7	0·47
0·6310	220·7	0·47
0·4812	237·9	0·47
0·4152	246·8	0·46
0·2933	269·4	0·47
	$\Lambda_0 = 385·0$	
3,4-Dihydroxybenzoic acid		
1·623	49·23	0·0323
1·130	58·30	0·0326
1·035	60·46	0·0323
0·8840	64·94	0·0323
0·6331	75·41	0·0324
0·5433	80·59	0·0323
0·5387	81·05	0·0322
0·4436	88·17	0·0325
0·3240	100·7	0·0324
0·2757	107·9	0·0326
0·2281	116·1	0·0322
	$\Lambda_0 = 370·6$	
2,5-Dichlorobenzoic acid		
0·8766	307·8	3·39
0·5145	329·7	3·50
0·4641	330·7	3·24
0·3938	338·7	3·59
0·3468	341·9	3·56
0·2157	351·4	3·40
0·1631	356·1	3·38
0·1539	356·4	3·25
	$\Lambda_0 = 373·9$	

Right column:

10^3C	Λ	10^3K
2,5-Dihydroxybenzoic acid		
2·687	180·1	1·11
1·624	212·4	1·13
1·430	219·6	$1·11_5$
1·087	237·1	$1·11_5$
1·075	238·3	$1·12_5$
0·9254	248·2	$1·13_5$
0·7338	262·4	$1·13_5$
0·5460	279·4	$1·12_5$
0·5357	279·7	$1·11_5$
0·4817	285·3	$1·10_5$
0·3535	302·1	$1·11_5$
0·2800	313·0	$1·11_5$
	$\Lambda_0 = 378·4$	
3,5-Dihydroxybenzoic acid		
1·607	80·17	0·0913
1·336	86·93	0·0915
1·056	96·13	0·0915
0·9917	98·67	0·0914
0·8279	106·4	0·0914
0·8276	106·5	0·0916
0·6968	114·2	0·0913
0·6494	117·5	0·0909
0·4760	132·9	0·0914
0·4215	139·3	0·0914
	$\Lambda_0 = 374·4$	
2,6-Dichlorobenzoic acid		
2·199	346·6	$24·9_5$
1·636	353·8	$26·0_5$
1·111	360·1	$25·6_5$
1·042	361·3	26·3
0·8238	364·4	26·8
0·6937	365·5	$24·4_5$
0·5340	367·9	24·2
0·4844	369·0	25·4
0·4062	370·1	$24·6_5$
0·3892	370·8	$26·5_5$
	$\Lambda_0 = 378·7$	

* This measurement was not used in the evaluation of Λ_0 or in calculating K.

such data for the present. Their use in structural considerations can be envisaged only after comparison with directly determined mobilities. The specific conductance of the water employed was 0·5—0·8 gemmho. Results are detailed in Table 2 (concentrations in moles l.$^{-1}$; Λ in mhos cm.^{2}).

[6] Dippy, Hughes, and Laxton, *J.*, 1954, 1470.
[7] Ives, *J.*, 1933, 731.
[8] Ives and Sames, *J.*, 1943, 511.