75. *Chemical Constitution and the Dissociation Constants of Monocarboxylic Acids. Part III.*

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The dissociation constants of a number of substituted benzoic acids have been redetermined, since earlier values are not now acceptable in view of the experimental and theoretical developments in the subject. The results are recorded in Table I, together with Λ_0 data. The practical methods and calculation of the results were those described in previous papers (Parts I and II; J., 1934, 161, 1888).

Table I.

Acid.	Λ_0 (Na salt).	Mean Λ_0 (acid).	$K_{\text{class.}} \times 10^5$.	$K_{\text{therm.}} \times 10^5$.
p-Fluorobenzoic	82·7, 83·5	382·7	7·39	7·22
o-Chlorobenzoic	84·5,* 84·6 *	384·1	119	114
m-Chlorobenzoic	80·75,* 81·25 *	380·6	15·2	14·8
p-Chlorobenzoic	82·3,* 82·3 *	381·9	10·7	$10{\cdot}5_5$
o-Bromobenzoic	80·2,* 80·8	380·1	146	140
p-Bromobenzoic	79·8,* 80·1 *	379·6	10·8	10·7
p-Aminophenylacetic	79·4, 80·4	379·5	(see Table III)	

* These values were obtained with solutions prepared from specimens of solid salt.

The following are earlier constants for aqueous solutions at 25° :

p-*Fluorobenzoic acid* : $K_{\text{class.}} \times 10^5 = 14$ (Slothouwer, *Rec. trav. chim.*, 1914, **33**, 324).

o-*Chlorobenzoic acid* : $K_{\text{class.}} \times 10^5 = 132$ (Ostwald, *Z. physikal. Chem.*, 1889, **3**, 418); 128—135 (Schaller, *ibid.*, 1898, **25**, 522; the value being erroneously ascribed to *p*-chlorobenzoic acid); 128 (Kendall, J., 1912, **101**, 1275); 121—138 (Whiteman and Jones, *Amer. Chem. J.*, 1911, **46**, 93); $K_{\text{therm.}} \times 10^5 = 119{\cdot}7$ (Saxton and Meier, *J. Amer. Chem. Soc.*, 1934, **56**, 1918).

m-*Chlorobenzoic acid* : $K_{\text{class.}} \times 10^5 = 15{\cdot}5$ (Ostwald, *loc. cit.*); 15·3—15·9 (Smith and Jones, *Amer. Chem. J.*, 1913, **50**, 28); $K_{\text{therm.}} \times 10^5 = 15{\cdot}06$ (Saxton and Meier, *loc. cit.*).

p-*Chlorobenzoic acid* : $K_{\text{class.}} \times 10^5 = 9{\cdot}3$ (Ostwald, *loc. cit.*); 7·8 (Smith and Jones, *loc. cit.*); $K_{\text{therm.}} \times 10^5 = 10{\cdot}4$ (Saxton and Meier, *loc. cit.*).

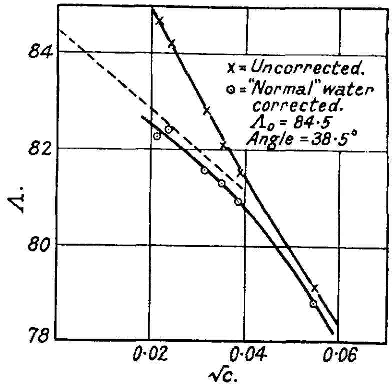
o-*Bromobenzoic acid* : $K_{\text{class.}} \times 10^5 = 145$ (Ostwald, *loc. cit.*); 140—180 (Smith and Jones, *loc. cit.*).

Values of $K_{\text{therm.}}$ for *o*-, *m*-, and *p*-chlorobenzoic acids were published by Saxton and Meier (*loc. cit.*) after the completion of our measurements. Those for the *m*- and *p*-acids agree with our values to within 2%, and even these small differences are capable of some explanation. In computing $K_{\text{therm.}}$ for the former acid, Saxton and Meier employed an extrapolation method; if, however, their value had represented the mean of the constants derived for the various concentrations (as in our procedure), a value of $1{\cdot}497 \times 10^{-4}$ would have been obtained. Their constant for the sparingly soluble *p*-acid was derived from two determinations only, and hence our value, the result of observations on *fifteen* solutions, is obviously more reliable. Ostwald's measurement was upon a single solution.

The Λ_0 (acid) values obtained for chlorobenzoic acids by Saxton and Meier are as follows: *o*-, 379·96; *m*-, 380·67. They did not conduct measurements on sodium *p*-chlorobenzoate, but accepted for Λ_0 (acid) the value accorded to benzoic acid; this provisional value is precisely the same as that obtained by us from actual measurements. Excellent agreement with Saxton and Meier is reached in the case of sodium *m*-chlorobenzoate, but with sodium *o*-chlorobenzoate there is a discordance, and this partly accounts for the 5·6% disagreement between the $K_{\text{therm.}}$ values. There is no question of differences in the accepted sodium- and hydrogen-ion mobilities, since Saxton and Meier also use MacInnes, Shedlovsky, and Longsworth's values (*J. Amer. Chem. Soc.*, 1932, **54**, 2758). Our method of computing Λ_0 (salt) was that described in Part II; the fig. shows a graph of measurements with sodium *o*-chlorobenzoate, the data being in Table II. Details for this salt are given in view of the aforementioned serious discordance.

One very significant feature of the present measurements is the order of strengths of the *p*-monohalogenobenzoic acids. This is Br>Cl>F, *i.e.*, the converse of the order exhibited by the halogenoacetic acids; the order of the constants for three *p*-halogenophenylacetic acids (Part I) was similar, *viz.*, I>Br>Cl. Measurements on *p*-fluorophenylacetic acid alone have since been conducted, and taking, for the present, a value of Λ_0 (acid) = 382, a thermodynamic constant of $5{\cdot}68 \times 10^{-5}$ is obtained, pointing to a relatively large fall in strength as in the case of *p*-fluorobenzoic acid (see Table I). There is every reason to believe that the final correct value for $K_{\text{therm.}}$ will not differ from the provisional value by more than 2%. This work provides the first conclusive demonstration of the inversion of the order of the halogens as shown in the strengths of aromatic carboxylic acids; the conclusion could not safely have been reached from the data available hitherto, even from the comparatively recent work of Kuhn and Wassermann (*Helv. Chim. Acta*, 1928, **11**, 31), who investigated all twelve monohalogenobenzoic acids in 50% aqueous methyl alcohol (see p. 346).

In the *o*-substituted benzoic and phenylacetic acids also, the bromo- is stronger than the chloro-acid, but perhaps more striking still is the fact that, although *o*-chloro- and *o*-bromo-benzoic acids are of the order of ten times as strong as their *m*- and *p*-isomerides, the monochloro- and monobromo-phenylacetic acids are all of comparable strengths.



The conductivity of *p*-aminophenylacetic acid has been measured because it was considered that it might be of use in connexion with the problem of amphoteric electrolytes. The values of $K_{\text{class.}}$, when arranged in the order of diminishing concentration of the solutions, present a steady fall until a concentration of about 0·0015*N* is reached; with further dilution an abnormal increase in acid strength occurs.

The Effect of Substituents on the Mobilities of Anions.—The only generalisations which can be made from the data of the 23 systems so far studied are that the methoxy- and nitro-substituted aromatic anions have relatively low speeds of migration, and also that the halogen- or nitro-substituted isomeric ions possess distinctly different speeds, dependent upon the position of the substituent.

EXPERIMENTAL.

The measurements, as hitherto, were conducted on aqueous solutions at 25°. Difficulty was encountered in preparing the initial stock solutions of the sparingly soluble *p*-chloro- and *p*-bromo-benzoic acids. Several hours' standing in the thermostat and vigorous intermittent shaking were necessary; this unavoidable delay did not have any effect. In the case of the above acids, and of *o*- and *m*-chlorobenzoic acids, 500 c.c. of initial solution were prepared (compare *p*-anisic acid; Part II). The time taken to dissolve different acids is not wholly dependent upon their maximum solubilities, since appreciably soluble substances dissolve at vastly different rates. In order to hasten complete solution, the specimens were always well pulverised in an agate mortar before weighing.

The solubilities of *p*-iodobenzoic and *p*-benzamidophenylacetic acids were so small as to preclude measurements.

Two expeditious items of procedure recently adopted by workers elsewhere are comparable with those employed by us. As an alternative to the weight-burette method of dilution, Brockman and Kilpatrick (*J. Amer. Chem. Soc.*, 1934, **56**, 1483) have followed a procedure in which a series of weighed flasks is required (compare Part I, p. 163). Also, Saxton and Meier (*loc. cit.*; cf. Saxton and Langer, *ibid.*, 1933, **55**, 1780), in their sodium salt investigations, prepared the solutions accurately by titration, and avoided the isolation of the solid salt; their choice of alkali (sodium carbonate), however, raises a definite objection.

TABLE II.

Sodium o-*chlorobenzoate.*

κ = 1·0 gemmho. Cell constant = 0·07243.

10^3 *C*	2·923	1·522	1·242	0·9575	0·5575	0·4421
Λ (uncorr.)	79·18	81·56	82·12	82·85	84·33	84·62
Λ (corr.)	78·83	80·91	81·36	81·68	82·45	82·35

TABLE III.

Cell constant.	10^3 *C*.	Λ.	$K \times 10^5$ (class.).	$K \times 10^5$ (therm.).
	p-*Fluorobenzoic acid.*			
0·07288	4·003	48·70	7·43	7·18
	2·250	63·52	7·43	7·22
	1·508	75·88	7·39	7·20
	0·9448	92·87	7·35	7·19
	0·5832	113·4	7·27	7·15
0·07288	3·468	52·14	7·45	7·21
	2·263	63·27	7·41	7·20
	1·718	71·27	7·32	7·13
	0·4657	124·3	7·27	7·15
	0·1730	181·2	7·36	7·27
0·07288	2·874	56·98	7·49	7·25
	1·812	70·33	7·50	7·30
	1·246	82·94	7·47	7·29
	0·7372	103·9	7·44	7·31
	0·2444	159·6	7·29	7·20
	m-*Chlorobenzoic acid.*			
0·07288	1·179	114·5	15·2	14·8
	0·8439	131·1	15·3	14·9
	0·7546	137·2	15·3	15·0
	0·5937	150·2	15·3	15·0
	0·4081	172·0	15·2	14·9
	0·1668	227·4	(14·8)	14·7
0·07288	1·203	113·4	15·2	14·8
	0·8139	132·4	15·1	14·8
	0·7000	140·5	15·1	14·8
	0·4910	161·4	15·3	15·0
	0·4162	170·7	15·2	14·9
0·07288	1·296	109·1	15·0	14·6
	0·8426	130·5	15·1	14·7
	0·7011	140·5	15·1	14·8
	0·5606	153·1	15·2	14·9
	0·5046	159·0	15·1	14·8
	o-*Bromobenzoic acid.*			
0·07305	3·413	181·3	149	142
	2·468	200·9	146	140
	1·199	247·3	145	142
	0·9356	263·6	147	(144)
0·07305	4·662	161·7	147	139
	2·776	193·2	146	140
	1·762	223·0	147	141
	0·7370	275·1	140	139
0·07305	5·077	159·3	(154)	(144)
	3·317	182·5	147	140
	3·280	182·6	146	139
	0·8360	269·2	144	142

Cell constant.	10^3 *C*.	Λ.	$K \times 10^5$ (class.).	$K \times 10^5$ (therm.).
	o-*Chlorobenzoic acid.*			
0·1367	6·011	138·0	121	114
	4·211	158·0	121	115
	3·529	168·6	121	115
	2·742	182·5	118	113
	1·640	214·2	116	112
0·1367	3·714	165·2	121	115
	2·856	180·5	119	114
	2·228	196·3	119	115
	1·507	220·9	118	114
0·07288	1·139	238·6	116	114
	0·5258	284·7	(112)	(111)
0·1367	2·947	178·8	120	115
	1·963	204·5	119	115
	1·238	234·0	118	115
0·07288	0·7084	267·7	114	112
	0·3261	309·1	(109)	(109)
	p-*Chlorobenzoic acid.*			
0·07288	0·3886	153·9	10·6	10·4
	0·3591	159·5	10·8	10·6
	0·3113	168·3	10·8	10·6
	0·2801	174·4	10·8	10·6
	0·2256	189·2	(11·0)	(10·8)
	0·1710	205·9	10·8	10·7
0·07288	0·3642	157·9	10·6	10·5
	0·3335	163·1	10·6	10·5
	0·2868	170·4	10·7	10·5
	0·2259	188·2	10·8	10·7
	0·1967	196·6	10·8	10·6
	0·1607	210·4	10·9	10·7
0·07288	0·3297	164·6	10·8	10·6
	0·3021	168·2	10·5	10·4
	0·2748	174·4	10·5	10·4
	0·2122	190·5	10·5	10·4
	0·1852	198·4	(10·4)	(10·3)
	p-*Bromobenzoic acid.*			
0·07288	0·2030	192·8	10·6	10·5
	0·1838	201·2	11·0	10·8
	0·1724	205·6	11·0	(10·9)
	0·1527	211·8	10·7	10·7
0·07288	0·1901	197·8	10·8	10·6
	0·1787	201·8	10·8	10·7
	0·1632	208·5	10·9	10·8
	0·1495	214·3	10·9	10·8
	0·1485	214·4	10·9	10·7
0·07288	0·1891	198·0	10·8	10·6
	0·1578	208·8	10·6	10·5
	0·1252	224·8	10·8	10·7

p-*Fluorophenylacetic acid.*

Cell constant.	10^3 *C.*	Λ.	*K* × 10^5 (therm.).
0·07243	1·943	60·71	5·69
	1·153	76·78	5·70
	1·000	81·51	5·66
	0·6995	94·81	5·62
	0·3518	126·0	5·63
	0·2031	153·8	(5·44)
0·07243	2·678	52·72	5·75
	1·602	66·71	5·77
	1·220	75·11	5·74
	0·8339	88·57	5·71
	0·5538	105·7	5·75
	0·4209	153·8	5·62
0·07243	0·8260	88·76	5·69
	0·5129	108·0	5·61
	0·2522	143·2	5·60
	0·1713	165·4	5·62

p-*Aminophenylacetic acid.**

Cell constant.	10^3 *C.*	Λ.	*K* × 10^5 (class.).
0·07355	3·084	10·99	0·267 (*a*)
	2·302	12·58	0·262 (*b*)
	2·209	12·87	0·263 (*c*)
	2·195	12·91	0·263 (*a*)
	1·714	14·34	0·255 (*b*)
	1·663	14·60	0·256 (*c*)
	1·493	15·21	0·250 (*a*)
	1·144	17·38	0·251 (*b*)
	1·131	17·56	0·254 (*c*)
	1·127	17·88	0·263 (*a*)
	0·8279	20·93	0·267 (*c*)
	0·8147	21·24	0·271 (*b*)
	0·7993	21·50	0·271 (*b*)
	0·6409	24·75	0·292 (*c*)

* In this case the three runs, *a*, *b*, and *c*, have been combined; no thermodynamic constants have been calculated, since the $K_{\text{class.}}$ values are themselves only apparent.

The values in parentheses were not included in the calculation of the averages given in Table I.

Preparation and Purification of Materials.—The chloro- and bromo-benzoic acids were all purchased from Messrs. British Drug Houses Ltd. Where the m. p.'s were below the best value recorded, preliminary crystallisations from water, sometimes containing acetone, were conducted, with animal charcoal if necessary. The final purification was carried out in the usual way with conductivity water. A variety of m. p.'s is given in the literature for most of these acids but, with one exception, each of our final specimens possessed the highest value.

o-Chlorobenzoic acid, 142° (Fels, *Z. Kryst.*, 1903, **37**, 485, 142°).

m-Chlorobenzoic acid, 158° (Montagne, *Rec. trav. chim.*, 1900, **19**, 52, 158°).

p-Chlorobenzoic acid, 241° (Fels, *Z. Kryst.*, 1900, **32**, 389, 243°; Müller, *Z. Chem.*, 1869, 137, 235°).

o-Bromobenzoic acid, 150° (Rhalis, *Annalen*, 1879, **198**, 102, 150°).

p-Bromobenzoic acid, 254—255° (Flaschner and Rankin, *Monatsh.*, 1910, **31**, 44, 254°).

Kuhn and Wassermann (*loc. cit.*) used all the above acids in their investigation, but the m. p.'s (uncorr.) recorded by them are consistently lower than ours. This deficiency, in addition to the fact that they did not carry out their measurements at one fixed temperature, doubtless contributes to the irregularity of their results.

p-Fluorobenzoic acid, m. p. 182°, was obtained by the hydrolysis of its ethyl ester (Dippy and Williams, J., 1934, 1466) (Slothouwer, *loc. cit.*, records m. p. 182°).

The preparation of *p*-fluorophenylacetic acid, m. p. 86°, has already been described (Dippy and Williams, *loc. cit.*).

p-Aminophenylacetic acid was obtained by the reduction of the *p*-nitro-acid with ferrous sulphate in the presence of ammonia (Jacobs and Heidelberger, *J. Amer. Chem. Soc.*, 1921, **43**, 180). After several recrystallisations from water (charcoal), the acid separated in almost colourless leaves, m. p. 200°. In earlier work the reduction was conducted far less successfully by the stannous chloride method.

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