148. *Chemical Constitution and the Dissociation Constants of Monocarboxylic Acids. Part V. Further Substituted Benzoic and Phenylacetic Acids.*

By J. Frederick J. Dippy and Reginald H. Lewis.

The investigation of the dissociation constants of monocarboxylic acids begun by Dippy and Williams (Parts I—III; J., 1934, 161, 1888; 1935, 343) was concerned mainly with monosubstituted (methyl, methoxyl, halogen, and nitroxyl) benzoic and phenylacetic acids, and had as its object the study of the polar influences of common substituents attached to the aromatic nucleus. The present work provides data for further members of these series of acids.

The following table sets out the Λ_0 data, and the mean classical and thermodynamic dissociation constants for the twelve newly examined acids. The last column records former determinations of $10^5K_{\text{class.}}$ for the benzoic acids. These data, extracted from the literature, relate to experiments embodying the older, less reliable technique; nowhere are thermodynamic constants recorded.

Our data for *m*- and *p*-toluic acids remove the doubt which existed regarding their relative strengths. The approximate constants for the *p*-acid due to White and Jones and to Schaller were much lower than that of Ostwald, who found the two acids to have identical strengths. It can now be accepted that the *p*-acid is decidedly the weaker.

Acid.	Λ_0 (Na salt).	Λ_0 (acid).	$10^5K_{\text{class.}}$.	$10^5K_{\text{therm.}}$.	Older values.
m-Toluic	79·3,* 80·1 *	379·3	5·47	5·35	5·6—5·7,[1] 5·14 [2]
p-Toluic	80·0,* 80·2 *	379·7	4·32	4·24	5·1,[2] 4·42,[3] 4·3—4·4 [1]
m-Methoxybenzoic	79·6,* 79·8 *	379·3	8·36	8·17	8·8 [4]
o-Fluorobenzoic	82·2, 83·25	382·3	55·7	54·1	30 [5]
m-Fluorobenzoic	82·1, 82·1	381·7	14·0$_5$	13·6$_5$	13·6,[2] 14 [5]
m-Bromobenzoic	80·2,* 80·6 *	380·0	15·7	15·4	13·7,[2] 15 [6]
o-Iodobenzoic	79·4, 79·8	379·2	139	137	132,[7] 137 [3]
m-Iodobenzoic	80·15, 81·05	380·2	14·2	14·1	16·3 [8]
m-Nitrobenzoic	83·1, 83·2	382·8	33·1	32·1	34·0,[9] 36·4 [3]
p-Nitrobenzoic	82·9, 83·2	382·7	38·5	37·6	39·6,[2] 40—43 [10]
o-Iodophenylacetic	77·0, 77·2	376·7	9·39	9·16	—
m-Iodophenylacetic	79·6	379·2	7·05	6·93	—

* These values were obtained with solutions prepared from the solid salts.

[1] White and Jones, *Amer. Chem. J.*, 1910, **44**, 184.
[2] Ostwald, *Z. physikal. Chem.*, 1889, **3**, 418.
[3] Schaller, *Z. physikal. Chem.*, 1898, **25**, 517.
[4] Pip, I.C.T., 1929.
[5] Slothouwer, *Rec. trav. chim.*, 1914, **33**, 324.
[6] Smith and Jones, *Amer. Chem. J.*, 1913, **50**, 1.
[7] Askenasy and Meyer, *Ber.*, 1893, **26**, 1354.
[8] Bethmann, *Z. physikal. Chem.*, 1890, **5**, 385.
[9] Euler, *ibid.*, 1896, **21**, 257.
[10] Wightman and Jones, *Amer. Chem. J.*, 1911, **46**, 90.

The new classical constant for *m*-fluorobenzoic acid is in harmony with those obtained previously, but that for the *o*-acid is almost twice as great as Slothouwer's. Our value for the *m*-bromo-acid is in reasonable agreement with that of White and Jones, and the present classical constants for the *o*- and *m*-iodo- and *m*- and *p*-nitro-benzoic acids differ considerably from the earlier values which, by comparison, are low for the first acid, and distinctly high for the other three.

The Measurement of Λ_0, *and the Mobilities of Ions.*—The method of computing Λ_0 has been described in Parts I—III, and illustrated by reference to sodium acetate and sodium *o*-chlorobenzoate. The plot of $\Lambda_{\text{uncorr.}}$ (and $\Lambda_{\text{corr.}}$) against $\sqrt{c}$ in each of these two cases yielded curves diverging perceptibly at concentrations of 0·0020—0·0015M, and the straight line possessing the Onsager slope approached nearer to the uncorrected than to the corrected curve. These observations hold true for the present sodium salt measurements; the form of the curves and the relative disposition of the Onsager straight line are reproduced from system to system in a strikingly consistent manner.

This method is necessarily somewhat approximate, since it represents an attempt to replace the usual tedious method of " solvent correction." Its use, however, has been fully justified in a repudiation of certain criticisms levelled at it (Dippy and Williams, *Chem. and Ind.*, 1935, **54**, 535).

On account of lack of material, measurement of only one " run " was made on sodium *m*-iodophenylacetate, and, as in previous cases, the isolation of the salts of the nitro-acids was impossible.

A fairly comprehensive survey of the mobilities of substituted benzoic and phenylacetic anions is now possible. In the main, they are decidedly lower than the mobilities of the unsubstituted ions; this to be expected on the grounds of increased size. For the same reason, the mobilities of the halogen-substituted anions are arranged, for the most part, in both series of acids in the order I $<$ Br $<$ Cl $<$ F. The size of the anion, however, does not seem to be the only factor affecting its movement; *e.g.*, the methoxyl substituent appears to depress abnormally the mobilities of benzoic and phenylacetic ions, and similarly for methyl in the benzoic ion. It is evident from the data that, on the subject of the mobilities of organic anions, only broad generalisations can be made.

Calculation of $\text{K}_{\text{therm.}}$.—Examination of the conductivity runs made on *o*-iodobenzoic acid (see tables) shows that at high dilutions $K_{\text{class.}}$ becomes smaller than $K_{\text{therm.}}$. It is the first instance of this feature encountered so far in this investigation, yet on the basis of the calculation it is to be expected in an acid of this order of strength. *o*-Nitrobenzoic acid should provide a still more pronounced example, for with stronger acids the differences become vast; *e.g.*, for iodic acid at 0·0005N, $K_{\text{therm.}} = 1{\cdot}8 \times 10^{-1}$ and $K_{\text{class.}} = 0{\cdot}5 \times 10^{-1}$ (see Davies, " The Conductivity of Solutions," 1933, p. 106).

EXPERIMENTAL.

The measurements were conducted on aqueous solutions at 25° as already described (Parts I—III). In order to eliminate as far as possible the shunt method of determining high resistances (2500 ohms), a Cambridge low-inductance decade resistance unit of 10,000 ohms (maximum) was added to the resistance arm of the bridge. The shunt method is now employed only in measuring the conductance of the solvent.

Since the last series of acids were measured, four new cells have been added to our complement, consequently two new cells are now reserved for salt solutions alone, and three for acid solutions. The electrodes of these cells are all coated with platinum black. The water is measured in a cell of low constant, possessing bright platinum electrodes. All the cells are of the bottle type described in Part I, and their characteristics are summarised as follows :

	Capacity (c.c.).	Electrodes. Area (sq. cm.).	Electrodes. Distance apart (cm.).	Approx. cell constant.
Acid cell 1	30	3·25	1·0	0·136
2	30	4·5	0·45	0·073
3	35	5·8	0·4	0·053
Salt cell 1	35	3·4	0·8	0·126
2	35	3·8	0·45	0·077
Water cell	40	7·2	0·35	0·039

Acid cell 3 was specially introduced for measurement of conductivity at very low concentrations. The area of the electrodes was greater than in the other acid cells, so as to provide a higher conductivity. It was found, however, that, when this cell was freshly introduced into a conductivity run for the purpose of measuring the last one or two solutions, values of *K* were obtained which were consistently lower than those secured with the other cells at higher concentrations. This was attributed to adsorption of the electrolyte on the platinum electrodes; it is conceivable that this effect should be negligible elsewhere, since, if adsorption is largely independent of the concentration of the solution, further removal of solute from solution should not occur after the electrodes have stood in the initial solution of the run. At comparatively high concentrations the effect of this adsorption must be exceedingly small, yet when a very dilute solution is involved it becomes appreciable. We therefore " inured " acid cell 3 by filling it with a solution of the appropriate acid (of roughly initial concentration) before using it on the very dilute solutions; after this treatment the cell was rinsed with water in the usual way. This process proved successful.

The stock solutions of the less soluble acids, *viz.*, *m*-bromo-, *m*-iodo-, and *p*-nitro-benzoic acids, were made up to 500 c.c. (cf. *m*- and *p*-chlorobenzoic acids, Part III), and all others to 250 c.c.

The observations made on the twelve acids are summarised in the tables, a typical run being given in each case. The water employed in making the solutions had a specific conductivity of 0·9—1·0 gemmho.

Materials.—*m*- and *p*-Toluic, *m*-bromo- and *m*-nitro-benzoic acids were purchased from British Drug Houses, Limited, *m*-iodobenzoic acid from L. Light and Co., and *p*-nitrobenzoic acid from Schering–Kahlbaum. The specimen of *m*-methoxybenzoic acid was kindly supplied by Dr. S. T. Bowden. Preliminary crystallisations were conducted with distilled water (and animal charcoal) until a steady m. p. was obtained. The *o*-iodobenzoic acid had first to be recrystallised from ether–acetone (9 : 1).

o- and *m*-Fluorobenzoic acids were prepared by the method of Dippy and Williams (J., 1934, 1466). Initial purification of the *m*-acid entailed conversion into the ethyl ester, purification of this by steam distillation, and hydrolysis with sodium hydroxide.

m-*Iodophenylacetic acid.* *m*-Iodobenzyl bromide (2 g.; 1 mol.) was heated with sodium cyanide (1 g.; 1·5 mols.) in alcohol (10 c.c.) on a water-bath for 5 hours. The oil obtained after evaporation of the alcohol was washed with water and heated with sulphuric acid (3 parts conc. acid; 2 parts water) for 20 mins. On cooling the clear liquid obtained after filtration through glass-wool, a solid separated which on recrystallisation from water (charcoal) yielded m-*iodophenylacetic acid*, m. p. 129° (Found: I, 48·0. $C_8H_7O_2I$ requires 48·5%) as colourless leaves (1 g.). *o*-Iodophenylacetic acid, m. p. 114°, was obtained (yield 40%) by a similar procedure.

We are indebted to Professor S. C. J. Olivier for the specimens of *o*- and *m*-iodobenzyl bromides.

Cell constant.	$10^3 C$.	Λ.	$10^5 K_{class.}$.	$10^5 K_{therm.}$.	Cell constant.	$10^3 C$.	Λ.	$10^5 K_{class.}$.	$10^5 K_{therm.}$.
m-*Toluic acid.*									
0·1373	2·525	51·96	5·49	5·35	0·07236	1·098	75·80	5·49	5·37
	1·659	62·33	5·36	(5·23)		0·7696	88·47	5·46	5·36
						0·4159	114·2	5·39	5·31
15 Determinations. Limits of $10^5 K_{therm.}$: 5·31—5·43.									
p-*Toluic acid.*									
0·1350	1·528	59·00	4·37	4·26	0·07236	0·5876	90·31	4·36	4·29
	1·082	68·98	4·37	4·27		0·4063	104·6	4·31	4·26
	0·7474	80·69	4·29	4·21		0·4031	105·5	4·25	4·20
17 Determinations. Limits of $10^5 K_{therm.}$: 4·19—4·29.									
m-*Methoxybenzoic acid.*									
0·1373	3·619	53·13	8·26	8·00	0·07236	0·9061	99·06	8·37	8·19
	1·747	74·74	8·46	8·23		0·8245	103·0	8·36	8·19
	1·222	87·96	8·56	8·35					
15 Determinations. Limits of $10^5 K_{therm.}$: 8·00—8·35.									
o-*Fluorobenzoic acid.*									
0·1367	4·124	121·3	(60·8)	(57·8)	0·07310	1·073	194·5	56·5	55·0
	1·980	156·5	56·2	54·2		0·8239	210·0	55·2	53·9
	1·385	177·5	55·8	54·0					
10 Determinations. Limits of $10^5 K_{therm.}$: 53·4—55·0.									
m-*Fluorobenzoic acid.*									
0·1363	3·658	68·23	$14{\cdot}2_5$	13·7	0·07316	1·046	115·3	$13{\cdot}6_5$	$13{\cdot}3_5$
	1·740	93·97	14·0	13·6		0·7492	133·6	14·1	13·8
	1·141	111·4	13·7	13·4		0·6205	142·7	$13{\cdot}8_5$	$13{\cdot}5_8$
14 Determinations. Limits of $10^5 K_{therm.}$: $13{\cdot}3_5$—13·9.									
m-*Bromobenzoic acid.*									
0·1363	1·343	110·3	15·9	$15{\cdot}4_5$	0·07311	0·7729	137·1	15·7	$15{\cdot}3_5$
	0·9024	128·5	15·6	$15{\cdot}2_5$		0·6637	145·5	$15{\cdot}7_5$	15·4
						0·5438	156·8	$15{\cdot}7_5$	$15{\cdot}4_5$
						0·3861	177·0	$15{\cdot}6_5$	15·4
16 Determinations. Limits of $10^5 K_{therm.}$: 15·2—15·45.									
o-*Iodobenzoic acid.*									
0·1375	2·344	201·2	141	$135._5$	0·07360	0·7161	275·7	139	$137._5$
	1·195	244·2	139	136		0·4531	300·9	138	$138._5$
	0·8688	263·9	$138._5$	$136._5$		0·3997	307·0	$137._5$	$138._5$
14 Determinations. Limits of $10^5 K_{therm.}$: $135._5$—$138._5$.									
m-*Iodobenzoic acid.*									
0·07236	0·3596	175·9	$14{\cdot}3_5$	14·1	0·05375	0·1912	216·1	14·3	$14{\cdot}1_5$
	0·2069	210·5	14·2	$14{\cdot}0_5$		0·09412	261·6	14·3	14·2
						0·08389	267·3	$13{\cdot}9_5$	13·9
14 Determinations. Limits of $10^5 K_{therm.}$: 139—142.									
m-*Nitrobenzoic acid.*									
0·1364	3·632	100·0	33·6	32·1	0·07305	1·040	163·1	32·9	32·0
	1·945	128·7	33·1	31·9		0·7800	180·9	33·0	32·2
						0·4979	208·9	32·7	32·1
16 Determinations. Limits of $10^5 K_{therm.}$: 31·5—32·5.									
p-*Nitrobenzoic acid.*									
0·1363	1·597	148·6	(39·4)	38·1	0·07319	0·7949	188·7	38·1	37·2
	1·021	173·5	38·4	37·5		0·7805	190·4	38·4	37·5
					0·05302	0·4742	221·4	(37·6)	37·0
15 Determinations. Limits of $10^5 K_{therm.}$: 36·9—38·1.									
o-*Iodophenylacetic acid.*									
0·1363	1·357	87·3	9·49	9·25	0·07311	0·6795	116·4	9·40	9·21
	0·8258	107·6	9·44	9·25		0·4506	137·4	9·44	9·31
						0·2530	169·0	9·25	9·13
19 Determinations. Limits of $10^5 K_{therm.}$: 9·00—9·33.									
m-*Iodophenylacetic acid.*									
0·1363	2·013	64·68	7·05	6·87	0·07311	0·4926	119·4	7·13	7·02
	1·145	83·26	7·08	6·92		0·3852	131·6	7·10	7·00
	0·7382	100·2	7·03	6·90		0·2197	162·5	7·07	6·97
11 Determinations. Limits of $10^5 K_{therm.}$: 6·86—7·02.									

Final purification of all acids was effected by means of conductivity water. The m. p.'s recorded below are those of the pure acids after storage; the values compare very favourably with the best in the literature.

Acid.	M. p.	M. p. (from literature).
m-Toluic	112·5°	111—113° (Auwers and Roth, *Annalen*, 1910, **373**, 245).
p-Toluic	181	181 (Ciamician and Silber, *Ber.*, 1912, **45**, 41).
m-Methoxybenzoic	110·5	110 (Ullmann and Uzbachian, *Ber.*, 1903, **36**, 1805).
o-Fluorobenzoic	127·5	124 (Cohen, J., 1911, **99**, 1063).
m-Fluorobenzoic	125	124 (Meyer and Hubner, *Monatsh.*, 1910, **31**, 934).
m-Bromobenzoic	155	155 (Holleman and de Bruyn, *Rec. trav. chim.*, 1901, **20**, 210).
o-Iodobenzoic	162·5	162 (Wachter, *Ber.*, 1893, **26**, 1744).
m-Iodobenzoic	189	187—188 (Cohen and Raper, J., 1904, **85**, 1273).
m-Nitrobenzoic	142	142 (Hubner, *Annalen*, 1884, **222**, 72).
p-Nitrobenzoic	241	240 (Fischer, *ibid.*, 1863, **127**, 137).
o-Iodophenylacetic	114·5	110 (Raum, *Ber.*, 1894, **27**, 3233).
m-Iodophenylacetic	129	

Sharp melting was observed throughout although slight softening invariably took place a few degress below the m. p. This seems to be a property of the aromatic acids studied so far; it certainly cannot be attributed to impurity.

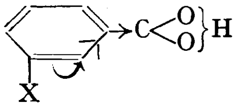
DISCUSSION.

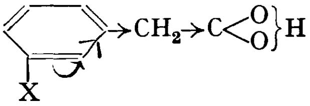
Reliable values for the thermodynamic dissociation constants in water of all the monohalogenobenzoic acids (except *p*-iodobenzoic acid, which is insufficiently soluble for measurement) are now available, and are summarised as 10^5K :

	F.	Cl.	Br.	I.
o-	54·1 †	114 *	140 *	137 †
m-	$13{\cdot}6_5$ †	14·8 *	15·4 †	14·1 †
p-	7·22 *	$10{\cdot}5_5$ *	10·7 *	—

* Recorded in Part III (*loc. cit.*). † Recorded in this paper.

The order Br > Cl > F for the above *o*- and *p*-series (and also for the corresponding phenylacetic acids, see Parts I and III), *i.e.*, the opposite of that to which operation of inductive effects would lead, has already been considered (Part IV; J., 1935, 346) in connexion with the data for other side-chain processes where a similar "inversion" has been observed. The whole problem has, moreover, been discussed comprehensively by Baddeley, Bennett, Glasstone, and Jones (J., 1935, 1827), who have provided additional data for the strengths of the halogeno-phenols and -anilines, and of certain reactions of halogeno-benzyl and -phenylethyl chlorides. Both they and Bettmann, Branch, and Yabroff (*J. Amer. Chem. Soc.*, 1934, **56**, 1865) have observed, in addition, irregularities in the effects of halogen substituents in the *m*-position, and our new results also make it clear that the strengths of the *m*-halogeno-benzoic and -phenylacetic acids, although not differing widely, are not in the order which would be anticipated on the basis of the inductive effects. Here again, therefore, there is some "compensating factor" decreasing in magnitude from fluorine onwards (the order first suggested by Baddeley and Bennett, J., 1933, 261); it may be suggested that this effect, whatever be its genesis, is relayed inductively from the *m*-position as follows :



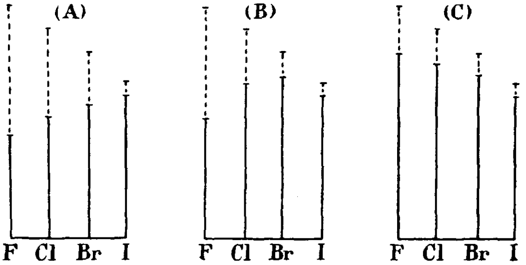


Bettmann, Branch, and Yabroff (*loc. cit.*) speak of "secondary resonance interaction" as the cause of inversion in the *m*-halogenophenylboric acids.

It was pointed out in Part IV that the effect superimposed upon the inductive effect need not of necessity cause a *complete* inversion in every instance; this is now illustrated by the fact that the iodo-acids in the *o*- and *m*-benzoic series fall out of the sequence. It is noteworthy, too, that in the *m*-substituted phenylacetic series, I < Cl. This point is made clearer by the figure, where A, B, and C show qualitatively three possible results of the combination of the two effects; the complete lines represent acid strengths if inductive effects alone operate, and the continuous portions represent the observed strengths.

Two further points of interest emerging from the work are (i) that although, in both benzoic and phenylacetic acids, halogen leads to the greatest increase in strength when in the *o*-position, there is no abnormal effect in phenylacetic as in benzoic acid; and (ii) that the *o*- and *p*-fluoro-acids in both series are markedly weaker than the other halogeno-acids.

The dissociation constant of *m*-toluic acid may now be taken to be definitely greater than that of its *p*-isomeride; this a further example of the order of effectiveness *p*-Me > *m*-Me > H, shown also in the strengths of phenols (Boyd, J., 1915, **107**, 1540) and anilines (Flürscheim, J., 1910, **97**, 96), and in numerous side-chain reactions (*e.g.*, 15 out of 16 listed by Williams, J., 1930, 37; compare Evans, Morgan, and Watson, J., 1935, 1178). The accurate value of $K_{\text{therm.}}$ now found for *m*-methoxybenzoic acid confirms the argument already given in Part IV (compare also the strengths of alkoxyanilines; Hall and Sprinkle, *J. Amer. Chem. Soc.*, 1932, **54**, 3469). The same remark applies to the values for *m*- and *p*-nitrobenzoic acids; further evidence is forthcoming from Williams's table of side-chain reactions (*loc. cit.*), the strengths of nitrophenols (Holleman and Herwig, *Rec. trav. chim.*, 1902, **21**, 444) and nitroanilines (Loewenherz, *Z. physikal. Chem.*, 1898, **25**, 405), and the halogenation of phenolic ethers and anilides (Jones, J., 1935, 1835). It is remarkable, however, that a *greater* relative difference is observed between *m*- and *p*-nitrophenylacetic acids (Parts I and II), and to explain this it may be suggested tentatively that hydrion arises from the methylene group of *p*-nitrophenylacetic acid, as is not impossible in view of the known reactivity of this group and the isolation of salts of suggested formula $CH(CO_2Et)\colon C_6H_4\colon NO\cdot OM$, by Opolski and Zwislocki (*Ber.*, 1916, **49**, 1606); in this connexion, measurement of the conductivities of the esters is desirable.



(A) I>Br>Cl>F, *e.g.*, the strengths of *p*-halogenophenylacetic acids.
(B) Br>Cl>I>F, *e.g.*, the strengths of *m*-halogenobenzoic acids.
(C) F>Cl>Br>I, *e.g.*, the tautomeric mobilities of *p*-halogeno-αγ-diphenylpropenes (Shoppee, J., 1930, 968).

The relationship of the thermodynamic dissociation constants to the dipole moments of the appropriate substituted benzenes has already been pointed out (Dippy and Watson, this vol., p. 436); a similar curve is obtained, as would be anticipated, if the moments of the substituted toluenes are employed. In the plot for phenylacetic acids (Dippy and Watson, *Chem. and Ind.*, 1935, **54**, 735) the point for the *m*-iodo-acid may now be inserted; this falls further from the curve than does that of the *m*-chloro-acid.

We wish to record our indebtedness to Dr. H. B. Watson for his continued interest in this work, and to Imperial Chemical Industries, Limited, for grants.

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