42. *Chemical Constitution and the Dissociation Constants of Monocarboxylic Acids. Part I. Some Substituted Phenylacetic Acids.*

By J. Frederick J. Dippy and Frank R. Williams.

The concepts underlying the application of electronic considerations to physico-organic problems have been based partly upon data of dissociation constants of organic acids and bases, the bulk of which were obtained by simple experimental means, and the use of Ostwald's method of deducing the constant. If electronic concepts are to be supported

and supplemented more accurately, it is necessary to employ modern experimental technique and to calculate from the data so obtained the "true" or thermodynamic dissociation constants by use of the Debye–Hückel–Onsager equation. In this series of investigations the dissociation constants of a number of monocarboxylic acids are being determined, and in order to cover an adequate field it has been necessary to employ methods which are expeditious but nevertheless reasonably accurate.

The calculation of the "true" dissociation constant of an electrolyte from conductivity data has followed the procedure advocated by Davies (*Trans. Faraday Soc.*, 1927, **23**, 351; "The Conductivity of Solutions," 1933, pp. 101—104; cf. Wolfenden, *Ann. Reports*, 1932, **29**, 28). The value of Λ_x, the sum of the mobilities of both ions in a solution of concentration C, is derived from the Onsager equation for an aqueous solution at 25°, *viz.*, $\Lambda_x = \Lambda_0 - (0{\cdot}2271\Lambda_0 + 59{\cdot}78)\sqrt{C_i}$, by means of Banks's approximation, $\Lambda_x = \sqrt{\Lambda_0^2 - 2b(\Lambda_0\Lambda C)^{\frac{1}{2}}}$ (J., 1931, 3341), where Λ and Λ_0 are the equivalent conductivities at concentration C and at infinite dilution respectively, and b is the Onsager slope. The true degree of ionisation Λ/Λ_x is next evaluated, and hence C_i and C_u, the true concentrations of ions and undissociated molecules respectively; by substitution in the equation $\log C_i^2/C_u = \log K + 2A\sqrt{C_i}$, the true dissociation constant, K, is then deduced. The value assigned to A, however, is the Debye–Hückel constant 0·505, and not the value of approximately 0·4 derived by Davies originally (*Phil. Mag.*, 1927, **4**, 244). During the last year, strong evidence has been adduced in favour of the former value (Hall, *J. Amer. Chem. Soc.*, 1932, **54**, 831; MacInnes and Shedlovsky, *ibid.*, p. 1429), and Davies has in consequence accepted it (*ibid.*, p. 1698).

The mobilities of the anions have been determined from conductivities of solutions of the sodium salts, prepared from specimens of the solid salts wherever possible. The equivalent conductivity at infinite dilution is evaluated (as suggested by Dr. C. W. Davies, private communication) by plotting $\sqrt{C}$ against uncorrected equivalent conductivity and also against equivalent conductivity to which the "normal" water correction has been applied; a straight line drawn between the curves so obtained is taken to represent the Onsager slope, the intercept of which on the Λ axis gives Λ_0. At least two values of Λ_0 are derived for each salt (see Table I). The sodium and hydrogen mobilities accepted for this work are 50·10 and 349·72 respectively (MacInnes, Shedlovsky, and Longsworth, *ibid.*, p. 2758). The average values of Λ_0 for the acids, calculated on this basis, are also given in Table I.

The following are the mean values of the "classical" or "Ostwald" and the "true" or "thermodynamic" dissociation constants, extracted from Table II. Values of the former found by earlier workers for three of the acids are included in brackets.

Acid.	$K \times 10^5$ (class.).	$K \times 10^5$ (therm.).
Phenylacetic	5·03 [5·56,[1] 5·02,[2] 5·05—5·45 [3]]	4·88
Diphenylacetic	11·7 [11·0 [4]]	11·5
p-Chlorophenylacetic	6·61	6·45
p-Bromophenylacetic	6·63	6·49
p-Iodophenylacetic	6·74	6·64
p-Nitrophenylacetic	14·6 [10·4 [5]]	14·1

[1] Ostwald, *Z. physikal. Chem.*, 1889, **3**, 241.
[2] Dittrich, cited by Stohmann and Schmidt, *J. pr. Chem.*, 1896, **53**, 345.
[3] White and Jones, *Amer. Chem. J.*, 1909, **42**, 520.
[4] Verkade, Diss., Delft, 1918.
[5] Basterfield and Tomecko, *Canadian J. Res.*, 1933, **3**, 447. This very low constant can largely be attributed to the abnormally high value of 414·18 for Λ_0 (acid) used by these workers in their calculations. For acids of this type Λ_0 invariably approximates to 380; recalculation of their results upon the basis of our Λ_0 value gives a mean constant of $12{\cdot}94 \times 10^{-5}$, although the individual values for the constant still show a great disparity.

The dissociation constants of further phenylacetic acids will be the subject of a second communication, and the combined data will then be discussed in the light of the electronic theory of valency and of the relationship observed by Nathan and Watson (J., 1933, p. 890) between the strength of an acid $CH_2X{\cdot}CO_2H$ and the dipole moment of CH_3X.

Experimental.

Measurement of Conductivity.—The bridge wire was of the straight metre type, provided with extension coils of about 4½ times the resistance of the wire. The variable resistance was a carefully calibrated, low-inductance Cambridge instrument (no ponderable correction was necessary) of the four-dial type, possessing a total resistance of 1111 ohms and capable of adjustment to 0·1 ohm. Two such instruments were available. When the resistance in the cell exceeded 2000 ohms a fixed resistance of 1000 ohms was inserted in parallel (cf. Shedlovsky, *J. Amer. Chem. Soc.*, **1932**, **54**, 1411). The symmetrical alternating current was generated by a Cambridge oscillator, adjusted to a frequency of 1000 c./sec., shielded in a metal-lined box connected to earth and situated at a convenient distance from the apparatus. The attainment of almost complete silence in the telephones (120 ohms) at the balance point indicated the absence of appreciable inductance and capacity effects in the circuit, and hence rendered unnecessary the use of a balancing condenser in the cell arm of the bridge.

The wire was calibrated for certain convenient points by means of the two Cambridge resistances inserted in the Wheatstone bridge circuit. In order to determine the point of balance during measurement of the resistance of a solution, the wire contact was fixed at one of the calibrated points and the Cambridge instrument used as the variable resistance. This method proved more satisfactory than the usual one of moving the sliding wire contact; moreover, a lengthy calibration of the wire was avoided, all that was needed before conducting each experiment being an examination of the resistance ratios for the specified points.

The cells were of the symmetrical bottle type somewhat similar in principle to those adopted by Ives and Riley (J., 1931, 1998). They were of about 30 c.c. capacity and were made in Jena glass 16 III. The platinum electrodes were spaced 2 cm. and 1 cm. apart in the case of the sodium salt cells, and 1 cm. and 0·5 cm. in the case of the acid cells. The last electrodes (0·5 cm.) had an area of 4·5 sq. cm., and were supported by glass struts to ensure their rigidity; the area of each of the other electrodes was 3·25 sq. cm. The cells were cleaned with nitric–chromic acid mixture, steamed thoroughly, and filled with conductivity water. The electrodes were platinised black in the usual manner, freed from impurity by the means suggested by Findlay ("Practical Physical Chemistry," 1931), and finally allowed to stand with conductivity water which was changed frequently. The leads were of copper wire amalgamated at the ends. They were connected to mercury cups immersed in the thermostat, and thence to the bridge as suggested by Washburn (*J. Amer. Chem. Soc.*, 1916, **38**, 2431).

For the cell-constant determinations Parker and Parker's specific conductivities of potassium chloride (*ibid.*, 1924, **46**, 312) were employed. "A.R." Potassium chloride was recrystallised twice from conductivity water, dried in a platinum dish at 100°, fused in an electric furnace, cooled, and stored in a clean glass vessel in a desiccator. The constant of the cell possessing electrodes 0·5 cm. apart was derived by the "intermediate cell" method (see Davies, *op. cit.*, p. 60). All constants were checked at frequent intervals, but no perceptible changes were recorded. The conductivity of the water used in general routine was $\kappa = 1{\cdot}2$—$1{\cdot}3$ gemmho; this was measured in a cell possessing bright platinum electrodes. The water thermostat was regulated to 25°, as recorded on a standardised thermometer.

The sodium salts were made in solution by treating the acids with equivalent quantities of sodium hydroxide (alcohol-crystallised "A.R." material). An approximately 0·01*N*-sodium hydroxide solution, made from water of known conductivity, was standardised by means of oxalic acid with phenolphthalein as indicator. The alkali was added from a Grade A burette until within about 2 c.c. of the end-point, titration being completed from a standardised pipette capable of being read to 0·01 c.c., and the end-point reading being taken as that immediately preceding the first drop to give the colour change; in all cases, one minute's drainage was allowed. To prepare a solution of the desired sodium salt the calculated amount of sodium hydroxide was added to a convenient weight of the acid contained in a weighed dry flask, calibrated to 200 c.c. at 25°; this was then placed in the thermostat and made up to the mark with further conductivity water at 25° (the specimen of water used throughout the preparation of any one solution was of known conductivity). The flask was next removed, dried, kept in the balance case for 20 minutes, and weighed; in this way the concentration of the solution was obtained in terms of wt./vol. and wt./wt. A portion of the prepared solution was always tested with indicator, no colour change taking place; upon the addition of a drop of diluted sodium hydroxide solution, however, the pink colour appeared.

To a number of weighed dry flasks calibrated to 100 c.c. at 25°, various quantities (approx. 5—60 c.c.) of the initial sodium salt solution were added; the flasks were then reweighed, and made up

to the mark at 25°, a number of successively dilute solutions of known concentration (wt./vol.) being thereby obtained. The sodium salts of phenylacetic, diphenylacetic, and *p*-bromo- and *p*-iodo-phenylacetic acids were isolated as solids by evaporating the initial salt solution to crystallisation in a platinum basin over a steam-bath (in the attempted preparation of sodium *p*-nitrophenylacetate the material repeatedly turned dark brown at this stage), cooling it, pouring off the supernatant liquid, and washing the crystals with absolute alcohol. This procedure was repeated twice, then the salt was dried at 110° in an air-oven and stored in a desiccator. A satisfactory sodium analysis was made upon each salt. Conductivity measurements made upon solutions prepared, on the one hand, from the solid salt, and, on the other, by proceeding without isolation of the salt, gave results in excellent agreement (cf. Kendall, J., 1912, **101**, 1275).

Solutions of the acids ranging from approximately 0·01*N* to 0·0002*N* were prepared by the same method of dilution as for the sodium salts. With diphenylacetic acid, which is very sparingly soluble, it was necessary to make up 500 c.c. of initial solution in order to permit of weighing a substantial quantity of the acid.

The balances employed were sensitive to 0·0001 g. The flasks were of Pyrex glass, and after being cleaned were seasoned for six months with conductivity water. Silk was used in the handling of all glass apparatus during weighing operations.

Conductivity measurements of both acids and salts were made upon each solution successively with diminishing concentration. The cell was prepared for each successive solution by first being drained and then kept with conductivity water; it was then rinsed, and kept in the thermostat with sufficient solution to cover the electrodes; this was repeated twice. The conductivities of the last two additions neither differed noticeably nor altered on standing for ½ hour. A method of filling similar to this has been described by Ives and Riley (J., 1931, 1998) and Ives (J., 1933, 731). No water correction was applied to the acid measurements.

Preparation of Materials.—*p*-Nitrophenylacetic acid, prepared by nitration of phenylacetic acid (Borsche, *Ber.*, 1909, **42**, 3596) and repeatedly crystallised from water containing a trace of acetone, had m. p. 152° (Found: equiv., 182. Calc.: 181).

p-Chlorophenylacetic acid was obtained by a method similar to that employed by Petrenko-Kritschenko (*Ber.*, 1892, **25**, 2239), further details being desirable. *p*-Nitrophenylacetic acid (40 g.) was reduced by heating with stannous chloride (160 g.) and concentrated hydrochloric acid (400 c.c.) in alcohol (320 c.c.) for 3 hours on a steam-bath. The solution was evaporated, treated with sodium hydroxide solution, and filtered. The filtrate was then slightly acidified, cooled to − 10°, and diazotised with 25% sodium nitrite solution. The product was added to hot cuprous chloride solution (10%) with stirring, steam distilled, and the residue extracted with ether. The solid (5·5 g.) obtained by evaporation of the dried ethereal solution yielded, upon repeated recrystallisation from water (charcoal), white needles of *p*-chlorophenylacetic acid (1·1 g.), m. p. 105° (Found: Cl, 20·7. Calc. for $C_8H_7O_2Cl$: Cl, 20·8%). Petrenko-Kritschenko (*loc. cit.*) did not isolate the acid but von Walther and Wetzlich (*J. pr. Chem.*, 1900, **61**, 195) give m. p. 105°.

p-Bromophenylacetic acid was prepared by hydrolysing *p*-bromobenzyl cyanide. Benzyl chloride (56 c.c.) was kept with bromine (28 c.c.) and iodine (0·5 g.) in the cold for 24 hours. The product was washed with 15% sodium carbonate solution and water, dried (sodium sulphate), and fractionated. The fraction of b. p. 220—250° yielded *p*-bromobenzyl chloride (55 g.; 60%) as white needles, m. p. 50°, b. p. 238° (Found: Cl, 16·7; Br, 39·9. Calc. for C_7H_6ClBr: Cl, 17·3; Br, 38·9%) (Boeseken, *Rec. trav. chim.*, 1904, **23**, 99, gives m. p. 41°, b. p. 236°; Errera, *Gazzetta*, 1888, **18**, 239, gives m. p. 38—39°).

p-Bromobenzyl chloride (6 g.) in alcohol (20 c.c.) was boiled under reflux for 3 hours with aqueous sodium cyanide (7 c.c. of 50% solution); the resulting oily layer was washed with water, and upon standing set to *p*-bromobenzyl cyanide, m. p. 47° (Lowery and Jackson, *Amer. Chem. J.*, 1881, **3**, 247, give m. p. 47°). Hydrolysis of the cyanide with sulphuric acid gave *p*-bromophenylacetic acid (4·5 g.), m. p. 114° (Lowery and Jackson, *loc. cit.*, give m. p. 114°; Robson, *Proc. Univ. Durham Phil. Soc.*, 1912, **4**, 225, gives m. p. 114—115°).

Small quantities of *p*-bromophenylacetic acid were prepared by direct bromination of phenylacetic acid (Bedson, J., 1880, **37**, 94), and by the diazotisation method; poor yields were obtained in each case. Satisfactory mixed melting points were derived from all specimens.

p-Iodophenylacetic acid was obtained from *p*-nitrophenylacetic acid by reduction and diazotisation, as for the preparation of the *p*-chloro-acid. To the diazotised solution potassium iodide was added in the presence of copper powder. The product was steam distilled, the residue extracted with ether, and the resulting black mass recrystallised first from benzene–

Table I.

Acid.	Λ_0 (Na salt).	Mean Λ_0 (acid).	Acid.	Λ_0 (Na salt).	Mean Λ_0 (acid).
Phenylacetic	80·7*; 80·7*	380·3	*p*-Bromophenylacetic ...	82·8 ; 83·2*	382·6
Diphenylacetic	75·4*; 75·4*	375·0	*p*-Iodophenylacetic	83·0*; 83·4	382·8
p-Chlorophenylacetic ...	83·2 ; 83·6	383·0	*p*-Nitrophenylacetic	78·1; 78·2; 78·3	377·8

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

Table II.

Cell constant.	$10^3 \times C$ (equivs./l.).	Λ.	$K \times 10^5$ (class.).	$K \times 10^5$ (therm.).	Cell constant.	$10^3 \times C$ (equivs./l.).	Λ.	$K \times 10^5$ (class.).	$K \times 10^5$ (therm.).
	Phenylacetic acid.					*Diphenylacetic acid.*			
0·1381	29·21	15·45	5·02	4·77	0·07207	0·2774	177·8	11·9	11·7
	13·17	22·60	4·94	4·74		0·2479	184·8	11·9	11·7
	7·715	29·33	4·97	4·79		0·2076	193·4	11·4	11·3
	3·560	42·27	4·95	4·80		0·1793	203·2	11·5	11·4
	1·761	59·14	5·04	4·92		0·1461	217·0	11·6	11·5
	1·310	66·66	4·88	4·78		0·1006	239·3	11·3	11·2
0·1381	6·536	32·31	5·16	5·00	0·07293	0·3283	168·3	12·0	11·8
	4·109	40·30	5·16	5·00		0·2898	175·8	12·0	11·8
	3·107	45·09	4·96	4·81		0·1886	201·5	11·8	11·6
	2·119	54·62	5·10	4·97		0·1516	215·4	11·8	11·6
	1·001	75·97	4·99	4·89		0·1127	234·1	11·7	11·6
	0·5636	97·52	4·99	4·90	0·07293	0·2840	174·7	11·5	11·4
0·1381	7·425	30·44	5·17	4·98		0·2482	184·9	11·9	11·8
	3·699	42·21	5·13	4·97		0·1700	206·5	11·5	11·4
	2·202	52·98	4·97	4·84		0·09806	244·0	11·9	11·8
	1·479	63·68	4·98	4·86		0·08305	251·1	11·3	11·2
					0·07293	0·2359	186·2	11·6	11·4
						0·2177	192·7	11·8	11·7
						0·1872	199·7	11·4	11·2
						0·1192	229·6	11·5	11·4
	p-*Chlorophenylacetic acid.*					p-*Bromophenylacetic acid.*			
0·07293	3·610	48·62	6·66	6·45	0·07293	2·875	54·62	6·83	6·63
	2·412	61·66	6·62	6·43		1·529	71·91	6·65	6·48
	1·116	82·12	6·53	6·38		1·089	83·56	6·63	6·49
	0·6243	104·9	6·43	6·33		0·4120	126·6	6·74	6·64
0·1381	3·971	47·01	6·82	6·60		0·1839	170·6	6·60	6·52
	2·078	62·77	6·68	6·50	0·1381	2·289	59·85	6·64	6·45
0·07293	1·206	80·58	6·74	6·60		0·8128	95·30	6·71	6·58
	0·8582	93·26	6·73	6·59	0·07293	0·5675	109·3	6·49	6·37
	0·3754	130·7	6·63	6·53		0·4198	126·0	6·65	6·54
0·1381	4·064	46·29	6·75	6·53	0·1381	1·806	66·51	6·60	6·41
0·07293	1·154	80·17	6·40	6·28		1·166	80·37	6·51	6·37
	0·6186	105·4	6·46	6·35	0·07293	0·7049	100·3	6·57	6·45
	0·4758	117·4	6·44	6·35		0·5509	111·1	6·54	6·43
	p-*Iodophenylacetic acid.*					p-*Nitrophenylacetic acid.*			
0·1381	1·217	81·04	6·92	6·76	0·1381	4·971	60·02	14·9	14·3
	0·6277	107·1	6·82	6·70		2·415	82·83	14·9	14·4
0·07293	0·3843	129·8	6·68	6·58		1·986	89·02	14·4	14·0
	0·2213	159·7	6·61	6·53		1·348	105·9	14·7	14·3
	0·1256	195·9	6·73	6·67		0·9926	117·9	14·1	13·8
0·07293	0·6080	108·7	6·84	6·72	0·1381	7·163	50·61	14·9	14·2
	0·3634	132·6	6·68	6·57		3·220	72·95	14·9	14·3
	0·3207	139·5	6·71	6·60		2·268	84·65	14·7	14·2
	0·2134	162·1	6·63	6·55		1·425	101·8	14·2	13·8
	0·1979	167·6	6·74	6·66		0·4894	157·6	14·6	14·3
0·07293	0·4948	118·5	6·87	6·75	0·1381	5·982	55·20	14·9	14·3
	0·2874	145·5	6·69	6·60		2·724	78·29	14·7	14·3
	0·1979	167·6	6·74	6·66		2·032	88·12	14·4	14·0
	0·1259	194·9	6·65	6·59		1·243	107·4	14·0	13·8

light petroleum (b. p. 80—100°) and then from water (charcoal); the *p*-iodophenylacetic acid formed white needles (10% over-all yield), m. p. 135—136° (Found: equiv., 262. Calc.: 262). Mabery and Jackson (*Ber.*, 1878, **11**, 55) give m. p. 135°.

Phenylacetic and diphenylacetic acids were both purchased.

All specimens of acids were finally purified further by recrystallisation three times from conductivity water, and stored for a prolonged period in a vacuum desiccator before use. The soundness of this procedure was proved in the case of *p*-chlorophenylacetic acid where a subsequent series of recrystallisations resulted in no change in conductivity results.

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