415. *Chemical Constitution and the Dissociation Constants of Monocarboxylic Acids. Part II.*

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THE investigation described in Part I * (this vol., p. 161) has been extended to other aromatic acids, and further details are now given of the means of evaluating the limiting anion mobility from data for the sodium salt.

The equivalent conductivities of solutions of the sodium salts (Λ, uncorr.), varying in concentration from 0·005 to 0·0004 equiv. per litre, are plotted against $\sqrt{C}$; the resulting curve becomes very steep at high dilutions. By plotting, in addition, the values of equivalent conductivity to which the " normal " water correction has been applied (Λ, corr.), a second curve is obtained which approximates to the first curve at higher concentrations but diminishes in slope as the concentration falls. The reason for this is that hydrolysis occurs, and therefore the necessary correction must be of smaller magnitude than the full " normal " correction (see Davies, *Trans. Faraday Soc.*, 1932, **28**, 607; Ives, J., 1933, 313). Typical curves referring to sodium acetate solutions are shown in the fig., the relevant data being included in Table II. At dilutions where the curves diverge (beginning at 0·0020—0·0012 equiv./l.), a straight line is drawn possessing the Onsager slope ($0·2271\ \Lambda_0 + 59·78$) which is calculated with sufficient accuracy from a roughly estimated value of Λ_0 obtained by inspection. The intercept on the Λ axis is taken to represent Λ_0. The angle of the Onsager

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* In Part I (p. 162, l. 12) the coefficient 0·2271 of the dissymmetry term in the Onsager equation for aqueous solutions at 25° was incorrectly copied as 0·2771, but the correct value was employed in actual calculations.

slope is 38—39° for the salts studied, and the positions of the two diverging curves in a system readily indicate the position of the straight line inclined at this angle. Values of Λ_0 obtained in this manner have proved reasonably reproducible. From the sodium acetate measurements, a mean value of 390·6 has been adduced for acetic acid, agreeing with that of MacInnes and Shedlovsky (*J. Amer. Chem. Soc.*, 1932, **54**, 1429), whose limiting mobilities of hydrogen and sodium have been accepted for this investigation (*ibid.*, p. 2758); Ives (J., 1933, 731) and Jeffery Vogel, and Lowry (*ibid.*, p. 1637) give 391·6 and 388·62, respectively. It must be emphasised that an important source of disagreement between Λ_0 (acid) values lies in the divergent values adopted for the limiting mobility of the hydrogen ion; *e.g.*, MacInnes and Shedlovsky use 349·72 and Jeffery and Vogel use their own value of 348·0.

Ives (*loc. cit.*) ascribes to benzoic acid a value of $\Lambda_0 = 379{\cdot}7$ whereas we find $\Lambda_0 = 383{\cdot}1$. Since the completion of this work, Brockman and Kilpatrick (*J. Amer. Chem. Soc.*, 1934, **56**, 1483) and Saxton and Meier (*ibid.*, p. 1918) have published values of 382·10 and 381·96 respectively.

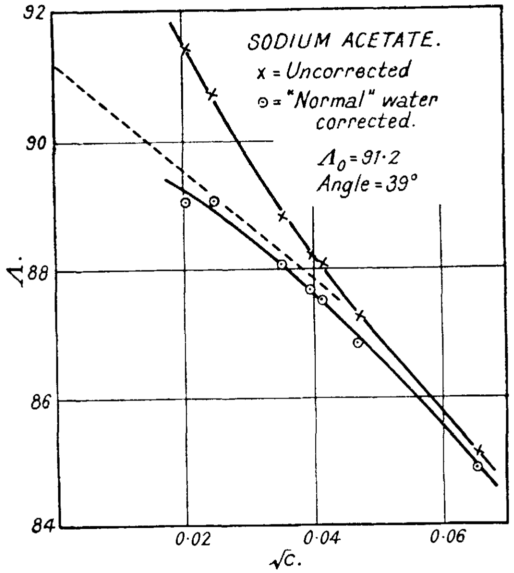

Table I sets out the individual Λ_0 (salt) and the mean Λ_0 (acid) values, together with the dissociation constants derived for the various acids, three of which have been studied by previous investigators. Only one determination of Λ_0 was made on each of the sodium salts of *o*- and *m*-chloro- and *p*-methoxy-phenylacetic acids owing to lack of material.

Table I.

Acid.	Λ_0 (Na salt).	Λ_0 (acid).	$K_{\text{class.}} \times 10^5$.	$K_{\text{therm.}} \times 10^5$.
o-Chlorophenylacetic	80·5	380·1	8·82	8·60
m-Chlorophenylacetic	80·3	379·9	7·38	7·24
o-Bromophenylacetic	80·3,* 80·5*	380·0	9·09	8·84
m-Nitrophenylacetic	81·3, 81·3	380·9	11·1	10·8
2 : 4-Dinitrophenylacetic	78·5, 79·0	378·3	32·3	31·5
p-Methoxyphenylacetic	78·8	378·4	4·45	4·36
3 : 4-Dimethoxyphenylacetic	77·6,* 78·0 *	377·4	4·74	4·64
p-Anisic	79·0,* 79·2 *	378·7	3·43	3·38
Benzoic	83·3,* 83·6 *	383·1	6·46	6·27
Acetic	90·8,* 91·2 *	390·6	1·81	1·76

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

Earlier constants ascribed to the last three acids are as follows: *Anisic acid*: $K_{\text{class.}} \times 10^5 = 3{\cdot}2$ (Ostwald, *Z. physikal. Chem.*, 1889, **3**, 369), 3·6 (Pip, *Diss.*, Heidelberg, 1898).

Benzoic acid: $K_{\text{class.}} \times 10^5 = 6{\cdot}0$ (Ostwald, *loc. cit.*), 6·69 (Euler, *Z. physikal. Chem.*, 1896, **21**, 257), 6·75—6·81 (Schaller, *ibid.*, 1898, **25**, 497), 6·07 (Dhar and Datta, *Z. Elektrochem.*, 1913, **19**, 407); $K_{\text{therm.}} \times 10^5 = 6{\cdot}7$ (Kolthoff and Bosch, *J. Physical Chem.*, 1932, **36**, 1695), 6·46 (Ives, Linstead, and Riley, J., 1933, 561), 6·527 (Ives, *ibid.*, p. 731). Other values are quoted in the text.

Acetic acid: $K_{\text{class.}} \times 10^5 = 1{\cdot}80$ (Ostwald, *loc. cit.*), 1·85 (Kendall, J., 1912, **101**, 1275), 1·95 (Dhar and Datta, *loc. cit.*), 1·813 (Jeffery and Vogel, J., 1932, 2829); $K_{\text{therm.}} \times 10^5 = 1{\cdot}785$ (Davies, *Phil. Mag.*, 1927, **4**, 249), 1·754 (Harned and Ehlers, *J. Amer. Chem. Soc.*, 1932, **54**, 1350), 1·752 (MacInnes and Shedlovsky, *ibid.*, p. 1429), 1·776 (Jeffery and Vogel, *loc. cit.*), 1·78 (Ives, Linstead, and Riley, *loc. cit.*), 1·759 (Ives, *loc. cit.*).

The measurements on acetic acid and its salt were conducted for control purposes, and the agreement with recent precision measurements indicates that the expeditious procedure adopted is trustworthy. Throughout the work the values of the individual constants were calculated initially to four significant figures, and for acetic acid they give a mean value of $K_{\text{therm.}} = 1{\cdot}756 \times 10^{-5}$ (cf. MacInnes and Shedlovsky; Harned, *locc. cit.*).

$K_{\text{therm.}}$ for benzoic acid, redetermined for reference purposes, is in good agreement with results recently published, *viz.*, $6{\cdot}295 \times 10^{-5}$ (Saxton and Meier, *loc. cit.*) and $6{\cdot}312 \times 10^{-5}$ (Brockman and Kilpatrick, *loc. cit.*); Vogel and Jeffery (*Chem. and Ind.*, 1934, **53**, 779) attributed the difference between the last value and theirs ($6{\cdot}373 \times 10^{-5}$) to the discordant hydrogen-ion mobility data employed (compare p. 1889).

Inspection of the results for the ten acids (Table III) shows that the difference between $K_{\text{class.}}$ and $K_{\text{therm.}}$ steadily diminishes as the solution becomes more dilute; a complete survey of these differences for all the measurements made on any given acid provides a useful check on the accuracy of the calculations involved.

It is noteworthy that, whereas substitution by the methoxy-group in the 4-position considerably diminishes the dissociation constants of benzoic and phenylacetic acids, the introduction of a second methoxy-group in the 3-position of *p*-methoxyphenylacetic acid causes a small increase in the constant of that acid. This favourable effect of a 3-alkoxy-group is noticeable in the measurements of Pip (*loc. cit.*) on *o*-, *m*-, and *p*-methoxy- and -ethoxy-benzoic acids; * the *o*- and, particularly, the *m*-isomerides, unlike the *p*-isomerides, are stronger acids than benzoic acid. Measurements on alkoxy-aromatic acids are being extended.

Discussion of all results from an electronic standpoint is postponed pending the completion of further work now in progress.

EXPERIMENTAL.

The conductivity method and technique have been described in Part I. All measurements were again made in aqueous solution at 25°. The water was obtained from a Vogel still (J., 1931, 1201), and had a conductivity of 0·8—1·1 gemmho. In the standardisation of the sodium hydroxide solution used in the preparation of the sodium salts, dry phenylacetic acid, purified as for conductivity measurements, was used in place of oxalic acid.

On account of the sparing solubility of anisic acid, 500 c.c. of the initial solution were made so as to permit of the weighing of a reasonable quantity of acid.

In the tables, concentrations (*C*) are given in g.-equivs./l.

TABLE II.

Sodium acetate.

$\kappa = 1{\cdot}0$ gemmho. Cell constant = 0·07243.

10^3 *C*.	Λ (uncorr.).	Λ (corr.).	10^3 *C*.	Λ (uncorr.).	Λ (corr.).
4·310	85·13	84·89	1·258	88·86	88·06
2·291	87·26	86·78	0·6146	90·78	89·17
1·704	88·12	87·56	0·4171	91·43	89·06
1·611	88·26	87·64			

TABLE III.

10^3 *C*.	Λ.	$K_{\text{class.}} \times 10^5$.	$K_{\text{therm.}} \times 10^5$.	10^3 *C*.	Λ.	$K_{\text{class.}} \times 10^5$.	$K_{\text{therm.}} \times 10^5$.	10^3 *C*.	Λ.	$K_{\text{class.}} \times 10^5$.	$K_{\text{therm.}} \times 10^5$.
o-*Chlorophenylacetic acid* (cell constant 0·07288).											
3·669	54·80	8·91	8·61	3·669	54·70	8·88	8·58	2·736	62·40	8·82	8·55
2·076	71·01	8·91	8·65	2·305	67·47	8·83	8·57	1·654	78·27	8·83	8·59
1·867	73·91	8·77	8·53	1·856	74·30	8·81	8·56	1·188	90·38	8·81	8·60
1·256	88·39	8·85	8·64	1·089	94·58	(8·98)	(8·77)	0·3426	149·7	8·77	8·63
0·6992	112·7	8·74	8·57	1·052	95·68	8·91	8·71				
0·6392	116·9	8·74	8·57	0·4655	132·6	8·71	8·56				
m-*Chlorophenylacetic acid* (cell constant 0·07288).											
1·849	69·01	7·46	7·25	1·961	66·94	7·39	7·20	2·158	64·34	7·45	7·24
0·8565	96·68	7·44	7·28	1·200	83·22	7·37	7·20	1·326	79·82	7·41	7·25
0·5716	114·1	7·36	7·25	0·9605	91·39	7·32	7·17	0·9473	92·43	7·41	7·26
0·3573	137·6	7·35	7·25	0·4448	125·9	7·30	7·19	0·5662	114·7	7·40	7·27
0·2653	154·5	7·40	7·29	0·2701	152·3	(7·25)	(7·14)	0·3119	145·2	7·38	7·28

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* The values of $K_{\text{class.}} \times 10^5$ for these acids at 25° are as follows: Methoxy-acids, *o*- 8·7, *m*- 8·8, *p*- 3·6; ethoxy-acids, *o*- 7·0, *m*- 9·0, *p*- 5·0 (see I.C.T., 1929).

TABLE III.—*Contd.*

$10^3 C$.	Λ.	$K_{\text{class.}} \times 10^5$.	$K_{\text{therm.}} \times 10^5$.	$10^3 C$.	Λ.	$K_{\text{class.}} \times 10^5$.	$K_{\text{therm.}} \times 10^5$.	$10^3 C$.	Λ.	$K_{\text{class.}} \times 10^5$.	$K_{\text{therm}} \times 10^5$.
o-*Bromophenylacetic acid* (cell constants : *a*, 0·1382; *b*, 0·07355).											
a 7·685	39·42	9·23	8·85	*a* 3·526	56·35	9·10	8·80	*b* 2·675	64·18	9·18	8·89
a 5·599	45·59	9·16	8·81	*a* 2·312	68·48	9·16	8·89	*b* 1·872	75·06	9·10	8·84
b 3·535	56·26	9·10	8·79	*b* 1·538	81·81	9·09	8·86	*b* 1·504	82·52	9·06	8·83
b 2·239	69·04	9·02	8·76	*b* 1·164	92·51	9·11	8·90	*b* 0·5369	127·2	9·04	8·88
b 0·6176	119·6	8·93	8·75	*b* 0·7802	109·5	9·10	8·90				
b 0·4987	130·8	9·01	8·86								
m-*Nitrophenylacetic acid* (cell constant 0·07355).											
5·712	49·68	11·2	10·7	4·723	54·34	11·2	10·8	4·543	55·24	11·2	10·7
3·894	59·23	11·2	10·8	3·535	62·16	11·3	10·9	2·813	68·66	11·1	10·8
2·983	66·88	11·1	10·8	2·280	75·63	11·2	10·9	2·251	75·33	11·0	10·7
2·274	76·00	11·1	10·9	1·750	84·76	11·1	10·8	1·610	87·42	11·0	10·7
0·8058	117·2	11·0	10·8	1·593	87·68	11·0	10·7	0·9048	111·3	10·9	10·7
0·3778	156·6	10·9	10·7					0·4535	146·2	10·9	10·7
2 : 4-*Dinitrophenylacetic acid* (cell constants : *a*, 0·07269; *b*, 0·07355).											
a 1·902	128·0	32·9	31·8	*a* 1·871	128·4	32·6	31·5	*b* 1·744	132·2	32·7	31·6
a 1·382	143·2	31·9	31·0	*a* 1·153	154·3	32·4	31·3	*b* 1·218	150·4	32·0	31·1
a 1·010	161·1	31·9	31·2	*a* 0·8153	175·1	32·5	31·8	*b* 0·9995	162·5	32·3	31·5
a 0·7456	180·7	32·6	31·8	*a* 0·2916	240·0	32·1	31·7	*b* 0·8143	174·1	32·0	31·2
a 0·6860	185·7	32·4	31·7					*b* 0·4740	209·0	32·3	31·8
p-*Methoxyphenylacetic acid* (cell constant 0·07288).											
2·787	44·99	4·47	4·35	2·424	48·07	4·48	4·37	2·534	46·94	4·45	4·34
1·579	58·52	4·47	4·37	1·469	60·30	4·44	4·34	1·460	60·71	4·48	4·38
1·182	66·71	4·46	4·37	1·081	69·33	4·44	4·35	1·121	68·22	4·44	4·36
0·8071	78·79	4·42	4·35	0·9439	73·89	4·47	4·38	0·7705	81·21	4·52	4·43
0·5960	89·84	4·40	4·33	0·2577	127·4	4·40	4·34	0 6504	87·24	4·49	4·41
0·4262	104·2	4·46	4·39					0·3079	119·9	4·52	(4·46)
3 : 4-*Dimethoxyphenylacetic acid* (cell constant 0·07288).											
2·076	52·90	4·75	4·63	3·816	39·70	4·72	4·58	1·187	68·45	4·77	4·67
1·946	54·61	4·76	4·65	2·236	50·90	4·70	4·58	1·059	72·02	4·76	4·67
1·356	64·52	4·78	4·67	1·751	56·99	4·70	4·59	0·5838	93·07	4·71	4·63
0·8523	79·25	4·76	4·67	1·477	61·73	4·72	4·62	0·1049	179·9	(4·56)	(4·53)
0·5010	99·88	4·77	4·67	0·4912	100·4	4·74	4·66				
p-*Anisic acid* (cell constant 0·07288).											
0·6857	75·37	3·39	3·34	0·7474	73·10	3·45	3·39	0·6869	75·94	3·44	3·39
0·6552	77·50	3·45	3·39	0·6767	76·26	3·44	3·38	0·6490	77·57	3·43	3·37
0·5104	86·50	3·45	3·40	0·6205	79·86	(3·50)	(3·44)	0·6050	80·42	3·46	3·41
0·4812	88·69	3·45	3·40	0·5503	83·68	3·45	3·40	0·5344	84·80	3·45	3·40
0·3702	99·59	(3·47)	(3·43)	0·4475	90·99	3·40	3·35	0·3028	107·7	3·42	3·38
0·3022	107·9	3·43	3·39	0·3695	98·68	3·39	3·35				
Benzoic acid (cell constants : *a*, 0·1367; *b*, 0·07355).											
a 7·711	33·60	6·50	6·25	*a* 5·607	39·19	6·54	6·30	*a* 7·413	34·29	6·52	6·27
a 4·418	43·89	6·55	6·33	*a* 3·567	48·39	6·51	6·30	*a* 4·766	42·01	6·43	6·21
a 2·907	52·81	6·41	6·21	*b* 2·677	54·94	6·43	6·24	*b* 2·147	60·96	6·47	6·29
b 2·038	62·19	6·41	6·24	*b* 1·927	63·77	6·41	6·24	*b* 2·136	61·06	6·45	6·28
b 1·841	65·22	6·43	6·26	*b* 1·395	74·11	6·47	6·33	*b* 0·9128	89·13	6·44	6·31
b 0·4688	117·9	6·41	6·30					*b* 0·5363	111·4	6·39	6·28
Acetic acid (cell constants : *a*, 0·1367; *b*, 0·07243).											
a 9·598	16·54	1·80	1·74	*a* 10·08	16·29	1·83	1·77	*a* 32·34	9·228	1·85	1·77
a 6·294	20·32	1·80	1·75	*a* 6·612	19·99	1·83	1·77	*a* 18·93	11·90	1·81	1·75
b 4·553	23·76	1·79	1·75	*a* 5·277	22·31	1·82	1·77	*a* 13·90	13·79	1·80	1·74
b 2·543	31·37	1·78	1·75	*b* 3·317	27·81	1·81	1·77	*a* 10·10	16·22	1·82	1·76
b 1·467	41·08	1·81	1·77	*b* 1·177	45·15	1·79	1·75	*a* 4·569	23·68	1·79	1·74

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

Preparation and Purification of Materials.—o-*Bromophenylacetic acid.* Bedson's details (J., 1880, **37**, 90) require amplification. Phenylacetic acid (10 g.) and mercuric oxide (9 g.) were triturated with water (75 c.c.) and immersed in ice, then bromine (3·7 c.c.) was added slowly with constant stirring. When reaction ceased, excess caustic soda was added and the mixture filtered. The filtrate was acidified with concentrated hydrochloric acid and the deposited solid, contaminated with *p*-bromophenylacetic and unchanged acids, was recrystallised repeatedly from light petroleum (b. p. 80—100°). Pure *o*-bromophenylacetic acid was thus obtained in colourless needles, m. p. 109° (4·5 g.) (Bedson records m. p. 103—104°) (Found : Br, 37·1. Calc. for $C_8H_7O_2Br$: Br, 37·2%). Oxidation of the acid with alkaline permanganate yielded *o*-bromobenzoic acid.

m-*Nitrophenylacetic acid.* Details of the preparation of this acid, m. p. 120°, by hydrolysis of *m*-nitrobenzyl cyanide (from *m*-nitrobenzyl chloride and sodium cyanide) will be published later. Gabriel and Borgmann (*Ber.*, 1883, **16**, 2064) record m. p. 117°, and Salkowski (*ibid.*, 1884, **17**, 504) m. p. 120°.

2 : 4-*Dinitrophenylacetic acid.* Nitration of phenylacetic acid (Borsche, *Ber.*, 1909, **42**, 1310) afforded this acid, m. p. 180° (Borsche gives 179—180°).

o- *and* m-*Chlorophenylacetic acids.* These acids (m. p.'s 96° and 76°, respectively) were kindly supplied by Professor G. M. Bennett, and *p*-methoxyphenylacetic acid (m. p. 86°) and ethyl 3 : 4-dimethoxyphenylacetate by Professor K. Kindler of Chemisches Staatsinstitut in Hamburg. The ester was hydrolysed to the corresponding (hydrated) acid; the anhydrous acid melted at 99° (Tiemann and Matsmoto, *Ber.*, 1878, **11**, 141, and Pictet and Gams, *ibid.*, 1909, **42**, 2943, give m. p. 98—99°).

p-Anisic acid (m. p. 184°) and benzoic acid (m. p. 121°) were purchased from British Drug Houses, Limited.

The acetic acid was purified by the method of Orton and Bradfield (J., 1927, 983). The accepted fraction froze at 15·95°, and the necessary correction for the retained water was made.

All the solid acids were finally recrystallised from conductivity water, and dried (see Part I).

The specimens were well authenticated both by m. p. and by the satisfactory equivalents found in each case. The m. p.'s recorded were those of the final specimens prior to measurement. Analyses of the sodium salts, conducted wherever practicable, proved corroborative.

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