43. *The Dissociation Constants of Organic Acids. Part VIII. Phenylacetic Acid.*

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The true dissociation constant of acetic acid is now known with some accuracy ($1{\cdot}764 \times 10^{-5}$, Part VII, J., 1933, 1637; $1{\cdot}753 \times 10^{-5}$, MacInnes and Shedlovsky, *J. Amer. Chem. Soc.*, 1932, **54**, 1429), but this acid, being liquid, and therefore difficult to prepare and keep in a state of purity, is not well suited for use as a standard in work involving a knowledge of this constant. A more suitable substance is phenylacetic acid, which is cheap, can be easily obtained in a state of high purity, and is fairly soluble in water. The conductivity of the acid, prepared by two distinct methods, over the range 0·0002—0·01*N*, has therefore been measured in silica cells, and that of the sodium salt in Pyrex cells over the same concentration range. The only previous determinations of conductivity are those on the acid by Ostwald (*Z. physikal. Chem.*, 1889, **3**, 270) and by White and Jones (*Amer. Chem. J.*, 1909, **42**, 520; 1910, **44**, 159) which must be regarded as approximate.

The results have been calculated as described in previous papers of this series (see Experimental). The mobility of the phenylacetate ion is 34·7, and the mean value of the thermodynamic dissociation constant is $4{\cdot}884 \times 10^{-5}$. The classical dissociation constant increases with rise of concentration, although the rate of increase at high concentrations is not so marked as in the more dilute solutions (see Table II); the mean value over the range 0·003—0·01*N* is $5{\cdot}068 \times 10^{-5}$.

A new series of standard buffer solutions is being prepared (and will shortly be described) with phenylacetic acid and its sodium salt. Since Prideaux and Ward use $5{\cdot}4 \times 10^{-5}$ for the dissociation constant of this acid in their universal buffer (J., 1924, **125**, 424), their p_H values require recalculation.

Experimental.

Preparation of Materials.—Phenylacetic acid; specimen 1. Kahlbaum's phenylacetonitrile, b. p. 112—114°/20 mm., was hydrolysed by refluxing with 15 times its weight of 18*N*-sulphuric acid for 6 hours, and the resultant acid recrystallised from benzene–light petroleum (b. p. 100—120°); m. p. 76·5—77°. *Specimen* 2. The commercial acid, m. p. 75—77°, was converted into the ethyl ester, b. p. 116—118°/20 mm., and the latter hydrolysed by refluxing for 12 hours with excess of alcoholic potassium hydroxide. The alcohol was distilled off, the acid precipitated by dilute sulphuric acid, and recrystallised twice as before; m. p. 76·5—77°.

Sodium Phenylacetate.—This was prepared by adding the calculated quantity of a standard solution of A.R. sodium hydroxide to a weighed quantity of the acid (*ex* nitrile), evaporating to a small bulk, and precipitating with alcohol. The salt was redissolved in water and, after concentration, reprecipitated with alcohol. This process was repeated twice (Found: Na, 14·52. Calc.: 14·56%). Owing to the hygroscopic character of the salt, the stock solution was prepared by weighing the solid directly into a large Pyrex weighing bottle containing a little conductivity water (compare benzenesulphonic acid, J., 1932, 411).

The general technique and apparatus employed was that described in earlier papers of this series. Four cells of the Hartley and Barrett type, two of silica, R ($0{\cdot}02586_3$) and Q ($0{\cdot}02674_8$), and two of Pyrex, S ($0{\cdot}03422_8$) and V ($0{\cdot}02781_5$), were used; the figures in parentheses are the corresponding cell constants. All the measurements were carried out at 25° ± 0·01°.

Solvent Correction.—No correction was applied to the acid solutions. For the sodium salt the solvent correction was calculated as follows. A normal solvent correction was first applied, *i.e.*, the specific conductivity of the water used was subtracted from the observed specific conductivity. This gave $\Lambda_0^n = 82{\cdot}52 = \Lambda_c + 109{\cdot}1C^{0{\cdot}564}$, and a preliminary value for the limiting mobility of the phenylacetate ion of 32·7, and Λ_0 for the acid = 348·0 + 32·7 = 380·7. Using the latter figure and the results for Run 1 on the acid, a preliminary value for $K_{\text{class.}} = 5{\cdot}123 \times 10^{-5}$ was obtained. The hydrogen-ion concentrations of the solutions were then calculated by means of the formula (9) (Part VII, J., **1933**, 1639); K_a was the preliminary value of the dissociation constant of the acid, and K_c, the primary dissociation constant of carbonic acid, was $4{\cdot}54 \times 10^{-5}$ (MacInnes and Belcher, *J. Amer. Chem. Soc.*, 1933, **55**, 2630). The combined solvent and hydrolysis correction was applied by means of equation (11) (*loc. cit.*); $\Lambda_{A'}$ was the preliminary mobility of the anion, $\Lambda_{H^{\cdot}}$ the mobility of the hydrogen ion (348·0), $\Lambda_{OH'}$ that for the hydroxyl ion (210·8, see Jeffery and Vogel, *Phil. Mag.*, in the press), and $\Lambda_{HCO_3'}$ that for the bicarbonate ion (46·9).

The results are tabulated below. For the sodium salt (Table I) κ is the specific conductivity

TABLE I.

Sodium Phenylacetate (M = 158·05).

$\Lambda_0^n = \Lambda_c + 134{\cdot}3\ C^{0{\cdot}527}$; $\Lambda_0^n = 84{\cdot}49$.
$\Lambda_0^s = \Lambda_c + 133{\cdot}9\ C^{0{\cdot}5}$; $\Lambda_0^s = 84{\cdot}60$.

$C \times 10^4$.	$\Lambda_{\text{norm.}}$.	$[H^{\cdot}] \times 10^7$.	$\Lambda_{\text{corr.}}$.	Λ_e.	$\Lambda_{\text{calc.}}$.	$C \times 10^4$.	$\Lambda_{\text{norm.}}$.	$[H^{\cdot}] \times 10^7$.	$\Lambda_{\text{corr.}}$.	Λ_e.	$\Lambda_{\text{calc.}}$.
Run 1. Cell S. κ=0·742.						Run 2. Cell V. κ=0·746.					
1·136	81·50	10·2	84·20	—	—	2·511	81·32	9·11	83·29	—	—
6·252	80·85	7·58	81·84	84·59	81·77	7·599	80·67	6·03	81·42	84·46	81·49
13·81	79·75	3·01	80·17	84·34	80·40	11·48	80·08	4·21	80·63	84·41	80·77
17·81	79·39	1·39	79·67	84·33	79·83	22·52	79·05	1·02	79·21	84·60	79·24
30·43	78·50	0·74	78·52	84·81	78·37	35·70	78·19	0·63	78·19	(85·07)	77·95
39·98	78·03	0·52	78·03	(85·61)	(77·45)	47·61	77·62	0·46	77·62	(85·62)	(76·81
57·50	77·31	0·42	77·31	(86·15)	(76·03)	67·49	76·80	0·32	76·80	(86·42)	—
80·69	76·51	0·29	76·51	(87·08)	(74·45)	99·98	75·88	0·20	75·88	(87·72)	—

TABLE II.

Phenylacetic Acid at 25° (M = 136·06).

$C \times 10^4$.	Λ_c.	$K_{\text{class.}} \times 10^5$.	$c'' \times 10^4$.	Λ_e.	$K' \times 10^5$.	$K_{\text{therm.}} \times 10^5$.
Run. 1 Specimen 1. Cell Q. κ = 0·806.						
3·469	119·53	(4·920)	1·0871	381·38	4·962	(4·844) *
10·41	75·21	(5·001)	2·0539	381·03	5·051	4·885
18·31	58·38	(5·026)	2·8064	380·80	5·079	4·885
35·32	43·15	5·060	4·0059	380·42	5·124	4·891
51·03	36·29	5·068	4·8705	380·18	5·139	4·882
66·18	32·06	5·071	5·5848	379·99	5·147	4·872
86·88	28·15	5·072	6·4392	379·74	5·155	4·870
Run 2. Specimen 1. Cell R. κ = 0·740.						
2·120	145·13	(4·909)	0·8064	381·48	4·950	(4·848)
5·737	97·12	(4·949)	1·4612	381·23	4·994	(4·855)
14·22	65·51	(5·028)	2·4456	380·91	5·080	4·898
26·29	49·49	5·061	3·4184	380·61	5·110	4·894
43·68	39·04	5·060	4·4841	380·29	5·130	4·884
60·01	33·61	5·074	5·3191	380·06	5·160	4·891
75·69	30·09	5·078	5·9955	379·87	5·158	4·872
104·1	25·81	5·086	7·0782	379·59	5·176	4·872
Run 3. Specimen 2. Cell Q. κ = 0·746.						
2·916	128·54	(4·950)	0·9825	381·40	4·993	4·879
16·29	61·61	(5·033)	2·6353	380·85	5·086	4·898
21·68	64·01	(5·027)	3·0758	380·70	5·085	4·882
30·77	46·03	5·060	3·7223	380·50	5·123	4·898
39·65	40·89	5·069	4·2626	380·35	5·135	4·894
62·40	32·99	5·074	5·4169	380·03	5·157	4·885
92·56	27·31	5·076	6·6574	379·70	5·227	4·888
	Mean	5·068			Mean	4·884

* The values in parentheses were not employed in the calculation of the mean.

TABLE III.

Equivalent conductivities at round concentrations.

$C\times 10^4$.	$CH_2Ph{\cdot}CO_2H$.	$CH_2Ph{\cdot}CO_2Na$.	$C\times 10^4$.	$CH_2Ph{\cdot}CO_2H$.	$CH_2Ph{\cdot}CO_2Na$.
2·0	135·0	—	50·0	36·52	77·50
5·0	104·0	82·06	60·0	33·66	77·09
10·0	79·8	80·95	70·0	30·89	76·83
20·0	55·32	79·47	80·0	29·41	76·42
30·0	46·51	78·53	90·0	27·67	76·16
40·0	40·74	77·98	100·0	25·95	75·88

of the water used, $\Lambda_{\text{norm.}}$ is the equivalent conductivity after application of a normal solvent correction, $[\mathrm{H}^{\cdot}]$ is the hydrogen-ion concentration of the solution, $\Lambda_{\text{corr.}}$ is the conductivity corrected by equation (11) (Part VII, *loc. cit.*), C is the concentration in g.-equivs. per litre, and Λ_0^n is the value of Λ_0 calculated by means of the " n " formula, the constants of which are given at the head of the table. The values of Λ_0^s and x deduced from the equation $\Lambda_0^s = \Lambda_c + xC^{0\cdot 5}$ are also indicated at the head of the table; " x " calc. is 79·2 and $\Delta = 42{\cdot}8\%$ (cf. J., 1931, 1720).

For the acid (Table II), $c'' \times 10^4$ is the ionic concentration corresponding to the molecular concentration C calculated as described in Part VI (J., 1932, 2837), two approximations being sufficient, Λ_e was obtained from the relationship $\Lambda_e CH_2Ph{\cdot}CO_2H = \Lambda HCl - \Lambda NaCl + \Lambda CH_2Ph{\cdot}CO_2Na$, K' is the dissociation constant computed from the corresponding degree of dissociation $\alpha = \Lambda_c/\Lambda_e$, and $K_{\text{therm.}}$ is the thermodynamic dissociation constant deduced from the equation $\log K_{\text{therm.}} = \log K' - 1{\cdot}010\, c''^{0\cdot 5}$.

The values of the equivalent conductivity at round concentrations (Table III) were interpolated from the Λ_c–C graph drawn with a flexible spline.

Correction.—The footnote in J., 1933, 1642 refers to the total concentration of un-ionised carbonic acid; the concentration of the bicarbonate ion must be added in order to obtain the total concentration of carbon dioxide in the water. The corrected values of the latter and the corresponding specific conductivity of the water are :—

κ, gemmho	0·2	0·4	0·8	1·0	2·0
$m\times 10^5$	0·108	0·329	1·117	1·678	6·196

Equation (7) on p. 1639 (*loc. cit.*) should read :

$$[\mathrm{H}^{\cdot}] = \mathrm{H}_1 + (s - \mathrm{H}_1^{4})/\mathrm{H}_1(2p\mathrm{H}_1 + q).$$

The authors thank the Royal Society and Imperial Chemical Industries for grants.

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[*Received, December 4th,* 1933.]