200. *The Thermochemistry of Solutions. Part V. The Heats of Ionisation of Some Organic Acids.*

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Using the calorimeter described in Part I (*J.*, 1934, 1362), the heats of ionisation of several organic acids have been measured in dilute solution over the temperature range 10—30°. The results have been combined with dissociation-constant data to give the thermodynamic functions for ionisation. The acids examined were: butyric, *iso*butyric, hexoic, *iso*valeric, β-chloropropionic, benzoic, *m*- and *p*-hydroxybenzoic, *m*- and *p*-nitrophenol, and *o*-chlorophenol. Less accurate data for *n*-valeric and trimethylacetic acids are also provided.

The object of the present paper is to present concisely the results of a series of thermochemical measurements made in 1938—1941 on the ionisation of some organic acids. The thermodynamics of acid–base equilibria continue to be the subject of active interest and controversy, and it is hoped that the data here set out will add to the reliable information available to test any theoretical treatments. The calorimetric measurement of heats of ionisation gives values which, for the concentration used, are comparable in accuracy with those derived from the temperature variation of dissociation constants as measured by the precise E.M.F. method of Harned and his collaborators (cf. Harned and Owen, " The Physical Chemistry of Electrolytic Solutions ", New York, 1943). The main uncertainty in the results is not the experimentally measured quantity, but its correction to infinite dilution, because of the well-known specificity of the heats of dilution of electrolytes. However, the heats have been measured at concentrations (M/20 or less) at which the heat of dilution corrections are fairly small, and where the limiting law furnishes at least a rough guide to their values.

The measurements were carried out at 10°, 20°, and 30° for all the acids except β-chloropropionic acid, which was only examined at 20° and 30°. The resulting heats of ionisation give the change in heat content of the reaction directly, and, when combined with free-energy data at one temperature, the value of the entropy change.

EXPERIMENTAL.

Calorimeter.—The calorimeter for heats of dilution and the general procedure described in Part I (*loc. cit.*) were used with a few minor modifications. For the measurements with butyric, *iso*butyric, *iso*valeric, hexoic, β-chloropropionic, benzoic, *p*-hydroxybenzoic, and most of those with *m*-hydroxybenzoic, the multiple-junction thermel described in Part IV (*J.*, 1939, 118) was used; for the remaining acids a thermel of slightly lower sensitivity but much lower thermal inertia constructed by D. McEwan was used.

In McEwan's thermel the ebonite formers employed in the previous design were eliminated. The rows of copper–constantan junctions were held in position by a framework of thin steel rods soldered at each end to a semicircular brass plate, and insulated from the thermel by lengths of insulation sleeving.

The heat capacity of the calorimeter was determined by carrying out the neutralisation of hydrochloric acid with sodium hydroxide, for which accurate values of ΔH have been given by Richards and Rowe (*J. Amer. Chem. Soc.*, 1922, **44**, 684).

Reaction Measured.—The reaction of which the heat content change was measured was

$$\mathrm{NaA + HCl = NaCl + HA} \quad \ldots\ldots\ldots \quad (1)$$

It was assumed that the sodium salt of the acid was completely dissociated; the heat change therefore corresponded to that of the reaction

$$\mathrm{A^- + H^+ = HA} \quad \ldots\ldots\ldots \quad (2)$$

plus that due to the dilution of the reactant in excess. A 10% excess of hydrochloric acid was used in order to suppress ionisation of the acid formed, and the solutions of the sodium salts contained between 2 and 3% of the free acid to ensure that there was no free alkali present. The values of ΔH_c recorded are those of the reverse of reaction (2), per mole. of acid, but they include the small contribution due to the heats of dilution.

Procedure.—25 Ml. of a solution of the sodium salt of the acid, generally 0·05M, were pipetted into the inner compartment of the calorimeter, 25 ml. of the hydrochloric acid solution into the outer compartment, and the temperature change on mixing determined as previously described. In some cases the concentrations had to be reduced because of the insolubility of the acid.

Materials.—The acids were pure commercial samples, further purified by distillation or crystallisation. Standard methods were used for the preparation of the sodium hydroxide and hydrochloric acid solutions.

Results.—To obtain ΔH from the observed temperature change, a knowledge of the specific heat of the resultant solutions is required. In many cases this was not available, but in view of the fact that they were all very dilute a value of 0·995 was adopted throughout. Only a small error is liable to be introduced by this approximation.

The results are given in Table I.*

TABLE I.

	Concn. of soltns.		ΔH_e (cals.).†			ΔH° (cals.).		
Acid.	Salt.	HCl.	10°.	20°.	30°.	10°.	20°.	30°.
Butyric …………	0·050	0·0555	−114 ± 5 (±4)	−392 ± 7 (±3)	−677 ± 10 (±3)	−242	− 542	− 853
*iso*Butyric ………	0·050	0·0555	−217 ± 6 (±4)	−473 ± 9 (±4)	− 745 ± 11 (±4)	−345	− 623	− 921
Hexoic ……………	0·050	0·0555	−69 ± 5 (±4)	−343 ± 6 (±3)	− 617 ± 10 (±4)	−197	− 493	− 793
*iso*Valeric ………	0·050	0·0555	−639 ± 10 (±4)	−889 ± 13 (±4)	−1126 ± 15 (±4)	−767	−1039	−1302
β-Chloropropionic	0·050	0·0555	—	−307 ± 7 (±4)	− 553 ± 10 (±4)	—	− 457	− 729
p-Hydroxybenzoic	0·0194	0·0215	1025 ± 33 (±23)	—	—	—	—	—
p-Hydroxybenzoic	0·0320	0·0352	—	681 ± 27 (±20)	307 ± 23 (±20)	945	561	167
Benzoic …………	0·0151	0·0172	694 ± 28 (±21)	—	—	—	—	—
Benzoic …………	0·0191	0·0215	—	389 ± 20 (±16)	41 ± 19 (±18)	622	295	−68
m-Hydroxybenzoic	0·0501	0·0566	785 ± 18 (±10)	501 ± 17 (±12)	149 ± 11 (±10)	655	348	−29
m-Nitrophenol …	0·0513	0·0566	5273 ± 69 (±16)	4984 ± 63 (±13)	4751 ± 62 (±14)	5145	4833	4575
p-Nitrophenol …	0·0515	0·0566	5023 ± 66 (±16)	4820 ± 61 (±13)	4642 ± 59 (±13)	4895	4669	4466
o-Chlorophenol …	0·0515	0·0566	5229 ± 68 (±16)	4946 ± 65 (±16)	4563 ± 60 (±14)	5101	4795	4387

† The total probable error is given immediately after the ΔH value. The figure in parentheses is the probable error due to random error from determination to determination.

The estimates of the error in ΔH_e were arrived at in the following way. The random error was obtained by means of an analysis of the results, grouping comparable experiments together, and applying Peters's formulæ to obtain the probable errors. Each ΔH value quoted is the mean of at least three determinations, the variation in the probable error from value to value being due to the fact that all the results are not the mean of the same number of observations. The probable error given in parentheses in Table I is the error obtained in this way. It was considered that systematic errors might be due to (*a*) error in the heat capacity of the calorimeter, (*b*) error in the specific heat of the solutions, (*c*) error due to inaccuracies in making up solutions. The effect of these errors is proportional to the temperature change, and a total of 1% of the observed ΔH values was allowed for them. The total uncertainty, taking both systematic and random errors into account, is given immediately after the ΔH values in the table. The values of ΔH°, the heat content change at infinite dilution, recorded are those obtained by applying the Debye–Huckel limiting law uniformly to all the electroytes present, and neglecting the heat of dilution of the undissociated acid; ΔH_D, the heat absorbed when an infinite quantity of solvent is added to a solution is given, for a uni-univalent electrolyte, by the expression

$$\Delta H_\mathrm{D} = \boldsymbol{N}\boldsymbol{e}^2\sqrt{\frac{8\pi \boldsymbol{N}\boldsymbol{e}^2}{1{,}000\epsilon \boldsymbol{k}T}}\cdot\frac{1}{\epsilon}\left(1+\frac{T}{\epsilon}\frac{\partial\epsilon}{\partial T}+\frac{1}{3}\frac{T}{V}\frac{\partial V}{\partial T}\right)\sqrt{c}$$

(cf. Fowler and Guggenheim, " Statistical Thermodynamics ", Cambridge, 1939, p. 404). Neglecting the term for the expansion of the solution, and inserting numerical values, we have $\Delta H = -398\sqrt{c}$, $-469\sqrt{c}$, and $-547\sqrt{c}$ cals. for temperatures of 10°, 20°, and 30°, respectively. These figures differ slightly from those given elsewhere (cf. Harned and Owen, *op. cit.*) because of the use of Wyman and Ingalls's data for the dielectric constant of water (*J. Amer. Chem. Soc.*, 1938, **60**, 1182) and the values of $\boldsymbol{N}$, $\boldsymbol{e}$, and $\boldsymbol{k}$ recommended by Birge (*Rep. Prog. Physics*, 1941, **8**, 90; see also *J.*, 1946, 219).

DISCUSSION.

The usefulness of the ΔH° values given in Table I for a discussion of the thermodynamic functions for ionisation of the acids is chiefly limited by the uncertainty of the Debye–Huckel correction. The deviations from the limiting law are, however, always of the same sign, and it is therefore reasonable to consider that the corrections applied represent a maximum, and that where the true value of ΔH° differs from that given, it lies nearer to the observed value of ΔH_e

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* Similar measurements carried out with *n*-valeric and trimethylacetic acids at 10°, 20°, and 30° were less reliable because of persistent temperature drifts. The plots of ΔH_e against T were not linear, ΔC_p appearing to decrease numerically with temperature. Although the data are not of comparable precision with that of those in the table, we think it worth recording that they lead to the following values of ΔH_e at 25° : *n*-valeric acid, − 520 ± 50 cals.; trimethylacetic acid, − 640 ± 100 cals.

at the concentration used. In his work on the heats of ionisation of some acids and bases at comparable concentrations, Pitzer (*J. Amer. Chem. Soc.*, 1937, **59**, 2365) also corrected his observed values to infinite dilution by means of the Debye–Huckel theory, and gives an estimate of the uncertainty of his final results, but does not given any clear indication of how it was derived. It does not appear possible to give a satisfactory estimate of the uncertainty of ΔH°, but it can be said that our values of the probable error of the observed quantity give a lower limit to the heat of ionisation, and that a comparison of the results with those obtained by making an estimate of the heats of dilution by analogy with experimental data for similar substances suggests that they are not in error by more than about 60 cals. Detailed consideration of the results for butyric acid suggests that our ΔH° values are rather more reliable at higher temperatures.

Values of ΔC_p have been obtained from the variation of ΔH° with temperature and these values, together with $\Delta S^\circ{}_{298\cdot 1}$ values obtained by combination of the results with dissociation-constant data, are given in Table II. The values of $\Delta H_{298\cdot 1}$ were obtained by interpolation; $\Delta C_{p298\cdot 1}$ is recorded. For those acids for which ΔC_p varies with temperature, ΔC_p at other temperatures may be obtained from the data in Table I. These values are discussed below.

TABLE II.

The thermodynamic functions for ionisation of some acids at 25° (in cals.).

Acid.	$\Delta C_p{}^\circ{}_{298\cdot 1}$.	$\Delta H^\circ{}_{298\cdot 1}$.	$\Delta S^\circ{}_{298\cdot 1}$.	$\Delta G^\circ{}_{298\cdot 1}$.	Lit. ref. for ΔG°.
Butyric	−30·6	− 698	−24·4	6,574	(1)
*iso*Butyric	−28·8	− 775	−24·8	6,622	(2)
Hexoic	−29·8	− 644	−24·5	6,648	(2)
*iso*Valeric	−27·0	−1168	−25·7	6,509	(2)
β-Chloropropionic	−27·2	− 593	−20·2	5,435	(3)
Benzoic	−35	110	−18·9	5,750	(4)
p-Hydroxybenzoic	−39	363	−19·8	6,270	(6)
m-Hydroxybenzoic	−38 *	159	−18·1	5,561	(5)
m-Nitrophenol	−26	4705	−22·1	11,280	(8)
p-Nitrophenol	−22	4570	−17·4	9,755	(9)
o-Chlorophenol	−41 *	4590	−23·5	11,580	(7)

* From 20° to 30°; the value from 10° to 20° is significantly different, and may be calculated from the ΔH° values in Table I.

References. (1) Harned and Sutherland (quoted by Harned and Owen, *op. cit.*). (2) Dippy (*J.*, 1938, 1222). (3) Dawson and Key (*Proc. Leeds Phil. Soc., Sci. Sectn.*, 1934, **2**, 296). (4) Rule and La Mer (*J. Amer. Chem. Soc.*, 1938, **60**, 1981). (5) Euler, quoted by Everett and Wynne-Jones (*Trans. Faraday Soc.*, 1939, **35**, 1380). (6) Jones and Speakman (*J.*, 1944, 19), calculated to 25° using our value of ΔH. (7) Murray and Gordon (*J. Amer. Chem. Soc.*, 1935, **57**, 110); this value is probably rather unreliable because the result was obtained in 50% methanol solution, and corrected to pure water on the assumption that the effect of methanol would be the same as its effect on the dissociation constant of phenol. (8) Lundén (*J. Chim. physique*, 1907, **5**, 574). (9) *Idem* (*Z. physikal. Chem.*, 1910, **70**, 249).

Aliphatic Acids.—Comparison with E.M.F. data is possible only for butyric acid, for which the thermodynamic dissociation constant K, has been measured from 0° to 60° by Harned and Sutherland (cf. Harned and Owen, *op. cit.*, Chap. 15). Their data give $\Delta H_{298\cdot 1}$ as − 693 cals., in excellent agreement with our value of − 698 cals. For ΔC_p, however, their results yield − 36·4 cals. per degree, compared with our value of − 30·6. Using our values of $\Delta H^\circ{}_{20^\circ}$ and ΔC_p, Harned's value for K_{20°, and the empirical equation (15 — 6 — 9) of Harned and Owen (*op. cit.*), we obtain values for K at 10° and 30° which agree with Harned's within his experimental error, as shown below, although use of our ΔC_p value outside this temperature range does not give agreement with Harned's dissociation constants. This suggests that our value of ΔC_p may be slightly too small, which could be accounted for if the deviations from the theoretical heat of dilution correction were greater at lower temperatures. In view of this, it seems reasonable to suggest that our numerical values of ΔC_p represent a lower limit.

	10°	20°	30°
10^5K, calc.	1·579	1·542	1·482
10^5K, obs.	1·576	1·542	1·484

Little comment on the values for the other unsubstituted aliphatic acids is necessary, except to point out that they confirm the general picture of the ionisation of fatty acids as discussed by Everett and Wynne-Jones (*loc. cit.*). It is noteworthy that for *iso*valeric acid, if we assume that the heat of dilution correction is zero at 10° and the full amount predicted by the limiting law at 30°, ΔC_p cannot be greater than -33, confirming that the fall in ΔC_p with increasing chain length, observed from formic to butyric acid, is real. β-Chloropropionic acid shows a markedly smaller entropy loss on ionisation, presumably because of its greater polarity (cf. Magee, Ri, and Eyring, *J. Chem. Physics*, 1941, **9**, 419).

Aromatic Acids.—For benzoic acid, Everett and Wynne-Jones (*loc. cit.*) have deduced from Schaller's data the values of 40 and $-36{\cdot}2$ for $\Delta H^\circ_{298\cdot1}$ and ΔC_p, respectively. The ionisation constant of benzoic acid has been measured at 5°, 25°, and 45° by Rule and La Mer (*J. Amer. Chem. Soc.*, 1938, **60**, 1981) and by applying Harned and Embree's empirical equation,

$$\log K - \log K_\theta = -p(t - \theta)^2,$$

with $p = 5 \times 10^{-5}$ which implies a value of -40 cals. per degree for ΔC_p (cf. Harned and Owen, *loc. cit.*), we obtained $\Delta H^\circ_{298\cdot1} = 191$ cals.* Our values of 110 cals. and 35 cals./degree are in good agreement with these results. For *m*-hydroxybenzoic acid, Everett and Wynne-Jones using Schaller's data give $\Delta H^\circ_{298\cdot1}$ as 170 cals. and $\Delta C_p = -29{\cdot}9$. Our value of 159 cals. for $\Delta H^\circ_{298\cdot1}$ is in excellent agreement, but we find that ΔC_p varies with temperature, being -31 from 10° to 20°, and -38 from 20° to 30°. The value quoted by Everett and Wynne-Jones is therefore almost certainly low.

Phenols.—Our result do not agree with the ΔH and ΔC_p values derivable from dissociation constants due to Lundén (*locc. cit.*) for *m*- and *p*-nitrophenol. His dissociation constants are from conductivity measurements, and they vary so widely with dilution that agreement with the present series is hardly to be expected. Our data are not sufficiently comprehensive to allow of a discussion on the influence of substituents on the thermodynamics of the ionisation of phenols.

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