161. *The Thermochemistry of Solutions. Part VII. The Heats of Ionisation of Some Substituted Ammonium Ions.*

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The heats of ionisation of the anilinium, benzylammonium, mono-2-hydroxyethylammonium, α-picolinium, and pyridinium ions have been measured calorimetrically at 10°, 20°, and 30°. The entropy and heat-capacity changes on ionisation have been calculated; the latter is unmistakably temperature-dependent in the case of the benzylammonium, α-picolinium, and pyridinium ions.

THE object of the present paper is to present concisely the results of a series of thermochemical measurements made in 1939—1941 on the ionisation of some positively charged acids of the substituted ammonium type. The energy changes associated with the " isoelectric " ionisation of such acids constitute one of the more puzzling chapters in the thermodynamics of acid–base equilibria (see, *e.g.*, Baughan, *J. Chem. Physics*, 1939, **7**, 951; Everett and Wynne-Jones, *Trans. Faraday Soc.*, 1939, **35**, 1380; *Proc. Roy. Soc.*, 1941, *A*, **177**, 499), and it is hoped that the thermochemical data below will amplify the somewhat limited body of quantitative information on which theoretical interpretations must be based.

The calorimeter and general technique previously described (Askew *et al.*, *J.*, 1934, 1362; Cottrell *et al.*, *J.*, (1948, 1019) were used. The heat evolved on the addition of hydrochloric acid to a solution of the amine was measured, the reverse of the process of ionisation. To prevent distillation of amine into the acid before the solutions were mixed, the inner compartment of the calorimeter (containing the amine) was covered with a film of vaselined cellophane, which was forced off when rotation of the calorimeter began. With the stronger bases (benzylamine and 2-hydroxyethylamine) precautions were necessary to eliminate errors due to the absorption of carbon dioxide by the amine, and to the heat evolved by the addition of protons to the significant concentration of hydroxyl ions in the solutions of such amines. The former error was eliminated by mixing an adequate excess of amine with the acid, and the latter by computing the heat evolution (of the order of 0·3% of the total), attributable to this side reaction.

The values of ΔH_c in Table I correspond to the reaction $BH^+ \longrightarrow B + H^+$, which is the reverse of the process carried out in the calorimeter. The concentration of the reactant solutions is also tabulated; the heat-content changes have not been corrected to infinite dilution, partly because of lack of heat of dilution data, and partly because both the limited experimental data (Streeck, *Z. physikal. Chem.*, 1934, *A*, **169**, 103) and the theoretical correction on the basis of the Debye and Huckel limiting law (Jackson *et al.*, *J.*, 1934, 1376) indicate that the correction is small and unlikely to exceed −40 calories per mole. Most values are the mean of at least four determinations, and none is based on less than three concordant results; the value of 0·995 has been assumed for the specific heat of the resultant solution in every case. The probable error of the mean values quoted is always less than 20 calories, but the absolute value of the heat of

TABLE I.

Ion.	Base, (moles/l.).	HCl, (moles/l.).	ΔH_c (cals./mole). 10°.	20°.	30°.	ΔC_p (cals./°c.). 10—20°.	20—30°.
Anilinium	0·06	0·054	+ 7,490	+ 7,370	+ 7,180	−12	−19
Benzylammonium	0·06	0·056	+13,160	+13,180	+12,995	+ 2	−18
2-Hydroxyethylammonium	0·06	0·054	+11,965	+12,050	+12,090	+ 8	+ 4
α-Picolinium	0·05	0·056	+ 5,930	+ 6,075	+ 6,115	+14	+ 4
Pyridinium	0·05	0·056	+ 4,130	+ 4,640	+ 4,800	+51	+16

ionisation is subject to a further uncertainty amounting to ±0·5%, owing to possible systematic errors in the heat capacity of solutions and calorimeter, and in the concentration of the solutions used. These systematic errors will not affect the values of ΔC_p and it is believed that the upper limit of uncertainty in these values is ±4 cals./°c.

If the correction to infinite dilution is neglected, values of ΔH_c at 25°, interpolated from the above data, can be combined with the thermodynamic dissociation constants of the ions concerned at 25° to compute the entropy change on ionisation at infinite dilution at that temperature. The uncertainty introduced by the approximation is probably no greater than that associated with the dissociation constants of at least some of the ions concerned (notably the α-picolinium ion) and the entropies of ionisation in Table II are probably well within one calorie/°K. of the true values.

TABLE II.

Ion.	*K*.	ΔG°_{298}.	ΔH^c_{298}.	ΔS_{298}.
Anilinium	$2{\cdot}54 \times 10^{-5}$ [1]	+ 6,265	+ 7,276	+3·4
Benzylammonium	$4{\cdot}26 \times 10^{-10}$ [2]	+12,777	+13,087	+1·0
2-Hydroxyethylammonium	$3{\cdot}55 \times 10^{-10}$ [3]	+12,882	+12,070	−2·7
α-Picolinium	$9{\cdot}6 \times 10^{-7}$ [4]	+ 8,210	+ 6,095	−7·0
Pyridinium	$4{\cdot}94 \times 10^{-6}$ [5]	+ 7,234	+ 4,721	−8·4

[1] Pedersen, *K. Danske Vidensk. Selskab. Skr.*, 1937, **14**, 9. [2] Carothers, Bickford, and Hurwitz, *J. Amer. Chem. Soc.*, 1927, **49**, 2908. [3] Glasstone, *J. Amer. Chem. Soc.*, 1947, **69**, 1213. [4] Guzman Barron, *J. Biol. Chem.*, 1937, **121**, 313. [5] Hahn and Klockmann, *Z. physikal. Chem.*, 1930, *A*, **146**, 373.

Discussion.—Little information is available with which the results tabulated above can be compared. In the first place, apart from very early calorimetric measurements at high concentrations, the anilinium and pyridinium ions are the only ones for which heats of ionisation can be calculated (from potentiometric data over a range of temperature). In the second place, even where accurate free-energy data are available, the process of differentiation (once for heat-content change and twice for heat-capacity change) is prone to lead to unreliable results, particularly where ΔC_p is significantly temperature-dependent.

For aniline, Pedersen (*loc. cit.*) obtained values of the dissociation constant at 15°, 25°, and 35°, with results indicating that ΔH° for the ionisation of the anilinium ion is independent of temperature over this range and equal to +7105 calories, a value which is not very different from our value at 30°. The apparent temperature-independence of the heat of ionisation is in sharp conflict with our results, but it is doubtful if much weight can be attached to a value of ΔC_p based upon free-energy data at only three temperatures. The potentiometric data of Hahn and Klockmann (*loc. cit.*) for pyridine cover a wider temperature range. However, the thermochemical values they have derived from their results are open to objection on grounds of internal consistency since they indicate for the basic ionisation of pyridine values of ΔC_p of +66 calories/°c. between 17·5° and 22·5°, and of −6 calories/°c. between 22·5° and 27·5°, whereas the basic dissociation constant is said to fit best an equation implying a temperature-independent value of ΔC_p of +36 calories/°c. A careful graphical analysis of their results suggests that they are compatible with a fairly wide range of values for the heat of dissociation of the pyridinium ion and indicate a value probably within 200—300 calories of 4000 at 25°.

The most significant aspect of these results is perhaps the conclusion that in the ionisation of at least three of the five ions studied, ΔC_p is definitely temperature-dependent; for such ionisation processes precise free-energy data over a wide temperature range will be the only adequate source of thermochemical data comparable in accuracy with those available by calorimetry. The correlation of the thermodynamic values with structure and the nature of the ionisation process must await the accumulation of experimental results for a wider range of substances.

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