## 204. *The Relative Strengths of Some Fatty Acids.*

By D. H. Everett and B. R. W. Pinsent.

Preliminary work on determinations of relative acid strength shows that, among the fatty acids, there are at least six cases of inversion of strength in the temperature range 15—45°. These observations confirm predictions based on the work of Tully and Levi on the heats of neutralisation of the acids concerned. Preliminary data are also given on the strength of trimethylacetic acid.

In recent years there has been some discussion regarding the validity of using ionisation constants, obtained in aqueous solution at a single temperature, as a basis for the theoretical interpretation of the relative strengths of acids. On the one hand (Hammett, *J. Chem. Physics*, 1936, **4**, 613; Baker, in Baker, Dippy and Page, *J.*, 1937, 1774; Everett and Wynne-Jones, *Trans. Faraday Soc.*, 1939, **35**, 1380; 1941, **37**, 373), it was realised that the way in which acid constants vary with temperature might lead to inversions in relative acid strength, and thus throw doubt on theoretical arguments based on data referring to a single temperature. Against this (Dippy, in Baker, Dippy, and Page, *loc. cit.*; Dippy, *J.*, 1938, 1222; *Chem. Rev.*, 1939, **25**, 151; Dippy and Jenkins, *Trans. Faraday Soc.*, 1941, **37**, 368) it was contended that no examples of inversion had been observed in the range of temperatures examined experimentally. In fact (Everett and Wynne-Jones, *loc. cit.*, 1941) some inversions within the experimental range were known, *e.g.*, among the first dissociation constants of the α-amino-acids; but it might be argued that these represent a special type of ionisation and that this behaviour is not general.

The heats of neutralisation of a series of acids in the temperature range 10—30° have been measured calorimetrically by Tully (Thesis, Oxford, 1939) and Levi (Thesis, Oxford, 1941), and these data, when taken in conjunction with Dippy's values for log $K_{25^\circ}$, suggest that inversions of acid strength should occur in the range 15—45° with the following pairs of fatty acids: acetic and *iso*valeric, propionic and *iso*butyric, propionic and *n*-valeric, propionic and *n*-hexoic.

We have made a direct comparison of the strengths of these pairs of acids by measurements of the e.m.f. of cells of the following type

$$\mathrm{H_2}\;\left|\;\begin{array}{l}0{\cdot}02\mathrm{N}\text{-}\mathrm{HA}_1\\ 0{\cdot}02\mathrm{N}\text{-}\mathrm{NaA}_1\end{array}\quad 0{\cdot}08\mathrm{N}\text{-}\mathrm{NaCl}\;\right|\;3{\cdot}5\mathrm{N}\text{-}\mathrm{KCl}\;\left|\;0{\cdot}08\mathrm{N}\text{-}\mathrm{NaCl}\quad\begin{array}{r}0{\cdot}02\mathrm{N}\text{-}\mathrm{HA}_2\\ 0{\cdot}02\mathrm{N}\text{-}\mathrm{NaA}_2\end{array}\;\right|\;\mathrm{H_2}$$

over a range of temperature. The buffer ratios and the total ionic strengths are identical in the two half-cells, so the total e.m.f. is given by

$$E = (2{\cdot}303\,\boldsymbol{R}T/F)\log_{10} K_{\mathrm{HA}_2}/K_{\mathrm{HA}_1}$$

the negative electrode being that in the buffer solution containing the weaker acid. The symmetry of this cell, especially when the acids $HA_1$ and $HA_2$ are very similar, reduces the overall liquid-junction potential to negligible proportions. Even when the two compartments contain widely different solutions, such as an amine buffer and hydrochloric acid (Everett and Wynne-Jones, *Proc. Roy. Soc.*, 1938, *A*, **169**, 190; 1941, *A*, **177**, 499), the liquid-junction correction is only a few tenths of a millivolt. The reliability of the technique for making the liquid junctions (cf. Unmack and Guggenheim, *Kgl. Dansk Vid. Selsk.*, 1930, **10**, 8) and their stability at various temperatures were checked by making up a completely symmetrical cell containing the same acetate buffer in both half-cells. At 20° the cell had an overall e.m.f. of 0·04 mv. Readings were then taken at 5° intervals up to 50°; the e.m.f. remained steady to ± 0·04 mv. throughout the experiment.

The relative dissociation constant, $K_r = K_{HA_2}/K_{HA_1}$, of a pair of acids is thus readily determined at a given ionic strength. A full examination of this technique will require measurements at a series of buffer concentrations and at several ionic strengths, but it seems unlikely that serious errors will be introduced in the relative constants between 0·10N and infinite dilution. This is confirmed by the agreement between the relative dissociation constants obtained in this work at 25°, and those calculated from Dippy's thermodynamic dissociation constants. Furthermore, Larsson and Adell (*Z. physikal. Chem.*, 1931, *A*, **156**, 352) have shown that for the fatty acids we have examined the activity coefficients at an ionic strength of 0·1N are constant to within about ± 2%.

## EXPERIMENTAL.

The acids employed were all purified samples: acetic acid was "AnalaR" grade; propionic was redistilled (b. p. 137·5°/760 mm.); *iso*butyric, redistilled (b. p. 153·4°/760 mm.); *iso*valeric, twice distilled (b. p. 170·6°/722 mm.); *n*-valeric, Kahlbaum; *n*-hexoic redistilled (b. p. 108·3—109·0°/25 mm.) and fractionally crystallised. Trimethylacetic acid was a pure synthetic preparation (b. p. 79°/20 mm.). Buffer solutions were prepared from carefully standardised solutions of the acids, and carbonate-free sodium hydroxide solution; the ionic strength was adjusted by addition of standard sodium chloride solution made from purified salt (Manov, Delollis, and Acree, *J. Res. Nat. Bur. Stand.*, 1944, **33**, 287).

Measurements of e.m.f. were made by means of a Tinsley vernier potentiometer and a recently standardised Weston cell. The e.m.f. cells and hydrogen saturators were similar to those used previously (Everett and Wynne-Jones, *locc. cit.*, 1938 and 1941).

The results are summarised in the table; the e.m.f.s have been corrected for small deviations of the actual buffer ratios from unity. Figures for the pair trimethylacetic–acetic acid are also included; no

$HA_1$ = Acetic acid;
$HA_2$ = *iso*valeric acid.

| Temp. | *E*, mv. | $K_r$. |
|---|---|---|
| 5·04° | +2·14 | 1·093 |
| 10·00 | +1·26 | 1·053 |
| 15·00 | +0·35 | 1·014 |
| 19·97 | −0·50 | $0·980_5$ |
| 25·00 | −1·32 | 0·950 |
| | | (cf. 0·952,* |
| | | 0·93 †) |
| 30·00 | −2·18 | 0·920 |

Inversion temp., 17·3°;
$\Delta H_r$ − 1155 cals./mole;
$T_m$‡ − 10°.

$HA_1$ = Acetic acid;
$HA_2$ = trimethylacetic acid.

| Temp. | *E*, mv. | $K_r$. |
|---|---|---|
| 25·00° | −16·61 | $0·533_0$ |
| | | (cf. 0·508 *) |
| 30·00 | −16·91 | $0·523_3$ |
| 40·00 | −18·40 | $0·505_6$ |
| 50·00 | −19·86 | 0·4899 |
| 60·00 | −21·41 | $0·474_2$ |

$\Delta H_r$ − 655 cals./mole;
$T_m$‡ + 3°.

$HA_1$ = Propionic acid;
$HA_2$ = *n*-valeric acid.

| Temp. | *E*, mv. | $K_r$. |
|---|---|---|
| 25·00° | +1·18 | 1·047 |
| | | (cf. 1·034,* |
| | | 1·12 †) |
| 30·00 | +0·89 | 1·035 |
| 35·00 | +0·55 | 1·021 |
| 45·00 | −0·03 | 0·999 |
| 50·00 | −0·34 | 0·988 |
| 55·00 | −0·58 | 0·980 |

Inversion temp., 44·4°;
$\Delta H_r$ − 445 cals./mole;
$T_m$‡ + 7°.

$HA_1$ = Propionic acid;
$HA_2$ = *n*-hexoic acid.

| Temp. | *E*, mv. | $K_r$. |
|---|---|---|
| 25·00° | +1·19 | 1·047 |
| | | (cf. 0·990,* 1·03 †) |
| 30·00 | +0·087 | 1·034 |
| 35·00 | +0·55 | 1·021 |
| 40·00 | +0·23 | 1·009 |

Inversion temp., 43·3°;
$\Delta H_r$ − 465 cals./mole;
$T_m$‡ + 7°.

$HA_1$ = Propionic acid;
$HA_2$ = *iso*butyric acid.

| Temp. | *E*, mv. | $K_r$. |
|---|---|---|
| 25·00° | +1·21 | 1·048 |
| | | (cf. 1·034,* 1·07 †) |
| 30·00 | +0·80 | 1·031 |
| 35·00 | +0·40 | 1·015 |
| 40·00 | 0·00 | 1·000 |
| 45·00 | −0·39 | 0·986 |
| 50·00 | −0·78 | 0·978 |

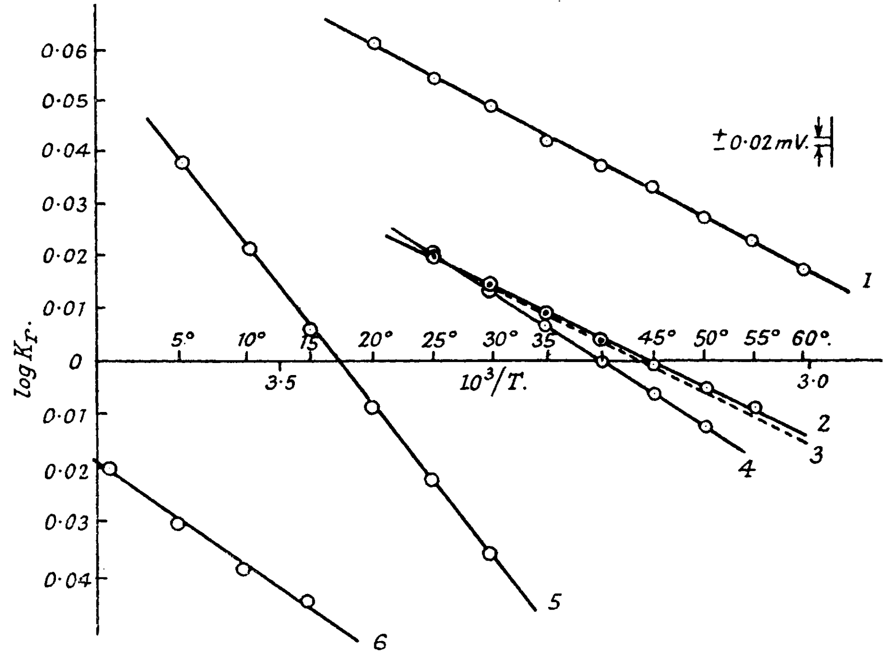
Inversion temp., 40·0°;
$\Delta H_r$ − 581 cals./mole;
$T_m$‡ + 4°.

* Dippy, *loc. cit.*, 1939. † Franke, *loc. cit.*
‡ Temperature at which log $K_2$ is a maximum.

inversion point was expected here, but it was of interest to determine the position of the maximum in the log $K$–$T$ curve of trimethylacetic acid. The table also contains values of $K_r$ calculated from Dippy's thermodynamic constants [taking $K_{\text{acetic}} = 1{\cdot}754 \times 10^{-5}$ and $K_{\text{propionic}} = 1{\cdot}335 \times 10^{-5}$ (Harned and Ehlers, *J. Amer. Chem. Soc.*, 1933, **55**, 652, 2379)] and from the classical dissociation constants of Franke (*Z. physikal. Chem.*, 1895, **16**, 477). The agreement between the various values is satisfactory, the largest deviation being for hexoic and propionic acid, where our value of $K_r$ is 6% higher than Dippy's value and nearly 2% higher than Franke's.

The figure shows log $K_r$ plotted against $1/T$; the inversions in strength are clearly demonstrated and the inversion temperatures are given in the table. Furthermore, both *n*-valeric and *n*-hexoic acid change their strength relative to *iso*butyric acid at about 26°. Harned's experimental data for the acid pairs butyric–propionic and butyric–acetic are also included in the figure. The lines obtained are straight within the limits of experimental error over the temperature range examined; their slope gives $\Delta H_r$, the difference $(\Delta H_2 - \Delta H_1)$ between the heats of ionisation of the two acids at the same temperatures, *i.e.*, the heat change accompanying the reaction $HA_2 + A_1 \longrightarrow HA_1 + A_2$. Experiments over a wider range would be required to determine to what extent $\Delta H_r$ varies with temperature.

*Logarithm of relative dissociation constant versus temperature.*



*Curve* 1, *Butyric–propionic* (*Harned*); 2, n-*valeric–propionic* (*open circles*); 3, n-*hexoic–propionic* (*black circles*); 4, iso*butyric–propionic*; 5, iso*valeric–acetic*; 6, *butyric–acetic* (*Harned*).

Approximate values (± 2°) of the temperature $T_m$ at which log $K$ (for acid 2) is a maximum were calculated knowing $T_m$ for acetic and propionic acid and assuming $\Delta C_p$ for the ionisation process to be − 35 cals./deg.-mole for all the acids considered.

## Discussion.

The data now presented show conclusively that inversions in the strength of the fatty acids do occur within the experimental range, and that other inversions may be expected in cases where dissociation constants differ by up to about 10% at room temperature.

A full discussion must await further more detailed work on the thermodynamics of these equilibria. Meanwhile we wish to make two points. (1) Our data indicate that for all the acids examined the temperatures ($T_m$) of maximum log $K$ are well below room temperature. The low value (+ 8°) shown by *n*-butyric acid, compared with 20—25° for the earlier members of the series, was regarded as a sign of the anomalous behaviour of this acid and was attributed by Dippy to hydrogen bonding between the terminal hydrogen atoms of the hydrocarbon chain and the carboxylate ion. This behaviour was also predicted for higher acids in the *n*-series. The fact that the low values of $T_m$ are also shown by *iso*butyric and trimethylacetic acids, in which this effect is not expected, suggests that some other interpretation is to be sought. (2) If rotation is strongly resisted in the butyrate ion we should expect this to be reflected in anomalous values for the entropy and heat capacity changes accompanying ionisation; there seems to be little evidence of such behaviour.

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PHYSICAL CHEMISTRY LABORATORY, OXFORD. [*Received, July 24th,* 1947.]