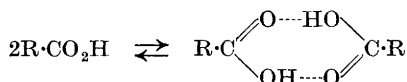


# THE ASSOCIATION OF CARBOXYLIC ACIDS

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## I. Introduction

THAT carboxylic acids are associated in some organic solvents and in the vapour has been known for more than seventy years, and this type of molecular association has recently been much investigated. The equilibrium between single and associated molecules has been experimentally studied, and a considerable body of quantitative data has accumulated. It has been found that in dilute solution (and probably also in the vapour state at low pressures) the equilibrium involves single and double molecules only. The structure of the dimeric molecule has been investigated by electron diffraction in the case of formic acid vapour.<sup>1</sup> It is generally recognised that in a dimer the two carboxyl groups are linked into a ring by hydrogen bonds :



The hydrogen bond in carboxylic acids appears from spectroscopic evidence to be stronger than that in alcohols, water, or phenol, as might be expected from the tendency of the carbonyl group to withdraw electrons from the hydroxyl group and so to weaken the O-H bond and increase its polarity. The dimerisation of carboxylic acids is thus a promising field for the study of hydrogen bonds, in that the equilibrium can be accurately measured for a series of related compounds, and the effect of substituents, as well as of solvent and temperature, systematically investigated. In this Review we shall try to summarise the experimental work on the association of carboxylic acids in the vapour phase and in solution, and to show how far the data can be interpreted in terms of intermolecular forces.

Hydrogen bonds cannot be regarded as covalent bonds involving bivalent hydrogen. From the theoretical point of view, this would need orbitals of much too high energy ; <sup>2</sup> and from the empirical point of view the heats of formation of hydrogen bonds are much less than those of covalent bonds. There is considerable evidence <sup>3</sup> that hydrogen bonds are predominantly electrostatic and can be regarded as due to the interaction of dipoles ; we shall see that there is evidence for this in the behaviour of carboxylic acids. It will be worth while to recall briefly the various accounts of the hydrogen bond that can be attempted : (a) An empirical description can be given

<sup>1</sup> (a) Karle and Brockway, *J. Amer. Chem. Soc.*, 1945, **67**, 898. (b) Schomaker and O'Gorman, *ibid.*, 1947, **69**, 2638 ; cf. also ref. 28b.

<sup>2</sup> Coulson, "Valence", Oxford Univ. Press, 1952, p. 301 *et seq.*

<sup>3</sup> M. M. Davies, *Ann. Reports*, 1946, **43**, 5.

in terms of dipole interaction. The interaction may be further interpreted in terms of valence theory by either of the two usual methods, giving accounts in terms of (b) molecular orbitals or (c) resonance.

(a) *Hydrogen bonds in terms of dipole interaction.* If we regard hydrogen bonds as essentially electrostatic, each hydrogen bond in a carboxylic acid dimer may be represented as due to the interaction of two dipoles :



The bond dipole moments of H—O— and O=C< are of the order of 1.6 and 2.5 D respectively,<sup>4</sup> so the electrostatic interaction at the observed O—O distance (about 2.7 Å) should be considerable. The hydrogen atom is unique in its small size, which allows the negatively charged end of a dipole to approach unusually close to the centre of positive charge, so that the electrostatic attraction is abnormally strong. This explains why other atoms do not allow the formation of similar bonds, and why esters, ethers, and alkyl halides are only weakly associated by comparison with carboxylic acids. Although electrostatic forces are in general undirected, it is usual for only two atoms to be linked by hydrogen bonds. This is due no doubt to the small size of the hydrogen atom which leaves no room for the approach of another atom; moreover, the electrostatic attraction is strongest along the line of the dipole. The account of the bond in terms of electrostatic attraction is thus able to explain the pronounced tendency to form a dimer with a definite structure.

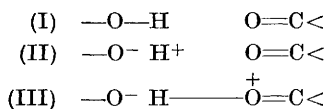
(b) *Molecular-orbital interpretation.* This empirical description of the properties of the bond is to be interpreted by valency theory. As usual, we can adopt either the molecular-orbital or the valence-bond (resonance) mode of approach. The hydrogen bond has been described in the language of molecular-orbital theory by Mecke,<sup>5a</sup> according to whom two steps are necessary in the formation of a hydrogen bond. Van der Waals forces loosen the O—H bond and as a result the proton "acquires quantum-mechanical bonding tendencies" to both partners (without taking up a symmetrical position between them). Mecke concludes that a hydrogen bond is formed if a hydroxyl group with an active hydrogen atom approaches a group with easily polarisable  $\pi$ -electrons. In molecular-orbital terminology the bonding due to electrostatic attraction is not distinct in principle from covalent binding; both involve a distortion of atomic or molecular orbitals and a resulting increase in molecular stability. No detailed calculations from molecular-orbital theory have been reported.

(c) *Resonance or valence-bond' interpretation.* The alternative interpretation, in terms of resonance, attributes the presence of dipoles to resonance between ionic and non-ionic structures or canonical forms, and any degree of polarity can be represented by suitably adjusting the relative contributions of these canonical forms to the resonance hybrid. Thus the polar

<sup>4</sup> Dewar, "Electronic Theory of Organic Chemistry", Oxford Univ. Press, 1949, p. 37.

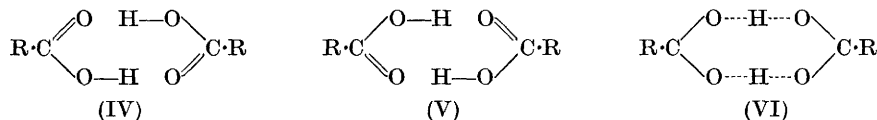
<sup>5</sup> (a) Mecke, *Z. physikal. Chem.*, 1950, **196**, A, 56. (b) Kellner, *Rep. Progr. Physics*, 1952, **15**, 1.

bond  $\text{—O—H}$  is represented as a resonance hybrid of the homopolar bond  $\text{—OH}$  and the ionic bond  $\text{—O}^- \text{H}^+$ , and the polar CO bond similarly as a hybrid of  $\text{>C=O}$  and  $\text{>C}^+ \text{—O}^-$ . In the hydrogen bonds involved in the dimerisation of carboxylic acids, the canonical forms to be taken into account include also a form involving a new covalent bond and a shift of charge from one oxygen atom to the other, and in the simplest model the most important canonical forms are given by Coulson<sup>2</sup> as including:



Estimates of the relative weights, or contributions, of these structures to the resonance hybrid can be made from a knowledge of the distances and dipole moments involved; they have been calculated in one case as 65, 31, and 4 respectively. Thus the contribution from the structure (III) involving the new covalent bond is small, and the first two forms, which give rise to the normal O—H dipole, predominate. The relative contributions of these two forms interpret the dipolar character of the bond in the language of resonance theory.

An earlier view in terms of resonance theory omitted all reference to ionic canonical forms, and consequently led to results at variance with experiment. The hydrogen bond was attributed to resonance between structures



(IV) and (V). The resulting resonance hybrid would be represented by (VI), in which the hydrogen atoms are symmetrically placed between the oxygen atoms and all the C—O bonds are alike. Infra-red spectroscopy<sup>6</sup> shows however that in dimers the hydrogen is not symmetrically placed, the O—H bond being in fact only slightly extended, and that the C—O bond frequencies are not all equal; electron-diffraction studies<sup>1</sup> also show that the C—O distances are unequal.

So long as the ionic canonical forms are taken into account, there is thus no sharp antithesis between the electrostatic and the resonance account of the hydrogen bond. We may, however, distinguish between electrostatic and "resonance" contributions to the energy of the bond, if by the latter we mean the contribution from the form (III), as distinct from (I) and (II) which involve no new covalent bond. It would be better to speak of electrostatic and covalence contributions, or to specify the canonical forms concerned, since resonance [between (I) and (II)] is involved in interpreting even purely electrostatic descriptions of the bond. The covalence contribution, as we have mentioned, appears from valency theory to be small; and calculations of the energy of the bond in terms of the electrostatic

<sup>6</sup> Davies and Sutherland, *J. Chem. Phys.*, 1938, **6**, 765.

energy due to the dipoles of OH and CO (and induced dipoles) give values of the right order. The electrostatic account thus appears *prima facie* to be an adequate approximation for discussions of the results obtained when the substituents, solvent, and other factors are varied.

## II. Association in the Vapour Phase

The association of a carboxylic acid under given conditions is most simply given quantitative expression in terms of the equilibrium constant. For the equilibrium between monomer ( $A_1$ ) and dimer ( $A_2$ ), which may be represented as  $A_2 \rightleftharpoons 2A_1$ , the equilibrium constant  $K_2$  in the gas phase may be expressed in terms of the partial pressures of monomer ( $p_1$ ) and of dimer ( $p_2$ ) as  $K_2 = p_1^2/p_2$ . This equilibrium constant measures the tendency of the dimer of a given acid to dissociate. Similar equations may be written for the higher polymers sometimes postulated. The use of partial pressures assumes that the vapour obeys the laws of a perfect gas mixture; for a non-ideal mixture, pressures should be replaced by fugacities. It is therefore desirable to use fairly low pressures, so that simple gas and equilibrium laws can be applied.

From the variation of the equilibrium constant with temperature, the changes of free energy ( $G$ ), heat content, and entropy on dissociation can at once be found. The standard free energy at a given temperature for the dissociation of the dimer is given by  $\Delta G_2^\circ = -RT \ln K_2$ ; the change of heat content ( $H$ ) may be found from the temperature-variation of  $K_2$ , since  $(\partial \ln K_2 / \partial T)_p = \Delta H_2^\circ / RT^2$ ; and the standard entropy change is given by  $\Delta S_2^\circ = (\Delta H_2^\circ - \Delta G_2^\circ) / T$ . The standard state is that at which all the partial pressures have the value unity (commonly, 1 atmosphere). Of these thermodynamic functions, the change in heat content,  $\Delta H_2^\circ$ , measures chiefly the energy of the bonds broken; and the change in standard entropy,  $\Delta S_2^\circ$ , will depend on the change in the number of molecules due to dissociation, whether this is simply a doubling, as in the gas phase, or whether, as in solutions, it also depends on a partial "freezing" of solvent molecules round the new monomer molecule. Measurements of the equilibrium constant are thus the normal experimental attack on the problem.

*Experimental methods for investigation of the gaseous equilibrium.* Investigation of the vapour-phase association of carboxylic acids dates back more than a hundred years, to work published by Bineau in 1846.<sup>7</sup> Since then, only three different techniques have been employed. Of these, investigation of pressure-temperature-volume relations by the Boyle's law type of apparatus has been the most popular; more recently vapour densities have been measured by means of the quartz microbalance. Infra-red spectroscopy has provided the third method of investigation.

Many of the early investigators measured the pressure-volume-temperature relations for a given mass of vapour in a bulb attached to a manometer, and so determined the apparent molecular weight of the carboxylic acid; but except in the work of Nernst and von Wartenberg<sup>8</sup> the results were

<sup>7</sup> Bineau, *Ann. Chim. Phys.*, 1846, **18**, 228.

<sup>8</sup> Nernst and von Wartenburg, *Z. Elektrochem.*, 1916, **22**, 37.

rather discordant. Later work has been more precise. Corrections have been made for adsorption by parallel experiments in vessels of differing surface : volume ratio,<sup>9, 10</sup> though high precision has also been claimed when this precaution has not been taken.<sup>11</sup>

Johnson and Nash<sup>12</sup> determined the vapour densities of aliphatic acids by means of a quartz microbalance. This balance was essentially a buoyancy globe counterpoised with a perforated bulb of equal surface area ; a small permanent electromagnet was sealed into the beam, and alteration of the current in an external electromagnet restored the beam to its reference position. This method has important advantages over the earlier technique in that it eliminates adsorption effects and does not require an estimate of the amount of material in the vapour phase. The results do, however, depend on a calibration, which requires a standard substance with a molecular weight in the higher part of the range to be studied. It will be interesting to see whether different investigators will obtain more concordant results by this technique than by the classical method (cf. Table 2, p. 261).

The use of infra-red spectroscopy presents different problems. Carboxylic acids show the characteristic O-H vibration absorption at about  $2.8 \mu$  only at higher temperatures, at which the acids are known to be monomeric. At lower temperatures, where dimerisation occurs, this band is replaced by one at about  $3.2 \mu$ , which is ascribed to the vibration of the hydroxyl group in the dimer. This method of measuring the relative concentrations has the defect that the band at  $3.2 \mu$  lies in the same region as that due to the C-H vibration, so that it is impossible to measure the degree of association by means of the fundamental frequency of the hydroxyl group participating in hydrogen-bond formation. If deuterated carboxylic acids,  $R\cdot CO_2D$ , are used, however, the frequency of the O-D...O vibration is lower by a factor of approximately  $\sqrt{2}$  and the absorption band appears at  $4.35 \mu$  and so can be measured. The O-H...O and O-D...O bands show a dependence on temperature ; as the temperature is increased, the fraction of the dimer increases and consequently the intensities of the O-H...D or O-D...O bands diminish and those corresponding to free O-H or O-D increase. Badger and Bauer<sup>13</sup> made the first attempt at quantitative measurements by investigating the temperature-dependence of the intensity of the second harmonic of the O-H band from acetic acid vapour. The results agreed roughly with MacDougall's vapour-density work,<sup>14</sup> but the accuracy was not very high because of the difficulty of making photographic determinations of the intensities. Herman and Hofstadter<sup>15</sup> used this method with considerable success in studying the dimerisation of deuterioacetic acid ; they observed the intensity of the O-D...O band over a range of temperature. In calculating the heat of association it was necessary to

<sup>9</sup> Coolidge, *J. Amer. Chem. Soc.*, 1928, **50**, 2166.

<sup>10</sup> Ritter and Simons, *ibid.*, 1945, **67**, 757.

<sup>11</sup> Taylor, *ibid.*, 1951, **73**, 315.

<sup>12</sup> Johnson and Nash, *ibid.*, 1950, **72**, 547.

<sup>13</sup> Badger and Bauer, *J. Chem. Phys.*, 1937, **5**, 839.

<sup>14</sup> MacDougall, *J. Amer. Chem. Soc.*, 1936, **58**, 2585.

<sup>15</sup> Herman and Hofstadter, *J. Chem. Phys.*, 1939, **7**, 460.

know the degree of association at one temperature ; this was obtained from the appropriate vapour-density data. To prove that the method was satisfactory, Herman<sup>16</sup> investigated the dimerisation of formic acid, using the temperature-dependence of an association band at  $7.35 \mu$ , and obtained results which were consistent with those for the deuterioacid. Several assumptions are made in applying this technique to the association of carboxylic acids,<sup>2</sup> and a previous knowledge of the system is required before the equilibrium constant can be evaluated, but on the whole the agreement with the two vapour-density methods is satisfactory, if the assumptions are accepted.

The ranges of temperature and pressure used by various investigators differ considerably, as may be seen from Table 1. The pressure is, however, always low enough for dimerisation to be the main equilibrium concerned. At higher pressures, several workers have found it necessary to postulate also either higher polymers or non-ideal behaviour to account fully for their results, as indicated in Table 2. These higher polymers are discussed below (p. 265).

TABLE 1. *Experimental conditions*

Acid	Investigator	Ref.	Pressure range (mm.)	Temp. range
H·CO <sub>2</sub> H . . .	Coolidge	9	3—1127	10—156°
„ . . .	Ramsperger and Porter	19	3—13	25—84
„ . . .	Taylor and Bruton	21	< 76	50—150
Me·CO <sub>2</sub> H . . .	MacDougall	14	5—25	25—40
„ . . .	Nernst and von Wartenburg	8	400—1500	40—200
„ . . .	Ritter and Simons	10	45—813	50—210
„ . . .	Johnson and Nash	12	160—1150	80—200
„ . . .	Taylor	11	13—34	50—150
Et·CO <sub>2</sub> H . . .	MacDougall	17	3—20	50—65
„ . . .	Taylor and Bruton	21	< 76	50—150
CMe <sub>3</sub> ·CO <sub>2</sub> H . . .	Johnson and Nash	12	98—780	115—200
Pr <sup>n</sup> ·CO <sub>2</sub> H . . .	Lundin, Harris, and Nash	18	250—720	141—200
n-C <sub>6</sub> H <sub>13</sub> ·CO <sub>2</sub> H . . .	„ „ „ „	18	200—280	189—227
CF <sub>3</sub> ·CO <sub>2</sub> H . . .	„ „ „ „	20	148—560	81—131

**Dimerisation.**—*Structure of the dimer.* Before dealing with studies on the equilibrium, it is useful to recall the results of electron-diffraction work on the dimeric forms of carboxylic acids. The earliest investigation was that of Pauling and Brockway in 1934 on formic acid ;<sup>21a</sup> they concluded that the dimeric species had a ring structure in which the C—O bonds were all of equal length, as in (VI). Karle and Brockway<sup>1</sup> confirmed the ring structure but concluded that the lengths of the two C—O bonds in the

<sup>16</sup> Herman, *J. Chem. Phys.*, 1940, **8**, 252.

<sup>17</sup> MacDougall, *J. Amer. Chem. Soc.*, 1941, **63**, 3420.

<sup>18</sup> Lundin, Harris, and Nash, *ibid.*, 1952, **74**, 743.

<sup>19</sup> Ramsperger and Porter, *ibid.*, 1926, **48**, 1267.

<sup>20</sup> Lundin, Harris, and Nash, *ibid.*, 1952, **74**, 4654.

<sup>21</sup> Taylor and Bruton, *ibid.*, p. 4151.

<sup>21a</sup> Pauling and Brockway, *Proc. Nat. Acad. Sci.*, 1934, **20**, 336.

carboxyl group were different, both in the monomer and in the dimer. Spectroscopic results in solution bear this out. In acetic acid the lengths were found to be the same as in formic. The O-O distance across the hydrogen bond was reported to be the same within a few hundredths of an Angstrom unit for formic, acetic, and trifluoroacetic acid, and there were no appreciable differences in the diffraction photographs of acetic and deuterioacetic acid. Although the interatomic distances in the formic acid monomer have been revised,<sup>1b</sup> the general picture of a ring structure for the dimers does not appear to be in doubt. Electron-diffraction studies tell us nothing directly, however, about the positions of the hydrogen atoms.

*Heats and entropies of dissociation of dimeric carboxylic acid molecules.* These quantities are of interest because, as has been mentioned, they reflect the energy of the bonds broken in dissociation and the changes in translational, rotational, and vibrational energy associated with the formation of the two new molecules. In the more recent investigations the temperature has usually been varied enough for evaluation of these factors. The temperature-dependence of the equilibrium constant  $K$  for dimerisation has commonly been expressed within experimental error by the equation  $\ln K_2 = A - B/T$ , where  $A$  and  $B$  are constants. The values of  $A$  and  $B$  give the heat of dissociation of the dimer,  $\Delta H_2^\circ (= B/R)$ , and the standard entropy change on dissociation,  $\Delta S_2^\circ (= A/R)$ . The results of various investigators are summarised in Table 2.

TABLE 2. *Standard heats and entropies of dissociation of dimers of aliphatic acids in the vapour phase*

From  $K_2$  in atm.; in the standard state, partial pressures are unity.

Acid	Method *	Ref.	Dimers		Higher polymers suggested †
			$\Delta H_2^\circ$ (kcal. mole <sup>-1</sup> )	$\Delta S_2^\circ$ (cal deg <sup>-1</sup> mole <sup>-1</sup> )	
H·CO <sub>2</sub> H . .	V.D.	9	14.1 <sub>2</sub>	36	—
” . .	V.D.	19	14.1	36	—
” . .	V.D.	21	14.1 ± 0.2	36.0	—
” . .	Spect.	16	12.4 ± 1	—	—
H·CO <sub>2</sub> D . .	”	16	12.8 ± 1	—	—
Me·CO <sub>2</sub> H . .	V.D.	8	15.0	—	—
” . .	V.D.	14	16.4 ± 0.8	41	—
” . .	V.D.	10	14.5 ± 0.4	35	Tetramer; $\Delta H_4^\circ$ 27
” . .	V.D.	12	13.8 ± 0.1	33	Trimer; $\Delta H_3^\circ$ 22.7
” . .	V.D.	11	15.3 ± 0.1	36.7	—
Me·CO <sub>2</sub> D . .	Spect.	15	15.9 ± 1	—	—
Et·CO <sub>2</sub> H . .	V.D.	17	18.5 ± 2	46	Trimer; $\Delta H_3^\circ$ 24
” . .	V.D.	21	15.2 ± 0.2	36.4	—
Et·CO <sub>2</sub> D . .	Spect.	15	14.1 ± 0.5	33	—
Pr·CO <sub>2</sub> H . .	V.D.	18	13.9 ± 0.2	33	Trimer; $\Delta H_3^\circ$ 23
Pr·CO <sub>2</sub> D . .	Spect.	15	13.8 ± 1	—	—
C <sub>6</sub> H <sub>13</sub> ·CO <sub>2</sub> H . .	V.D.	18	13.4 ± 0.7	—	—
CMe <sub>2</sub> ·CO <sub>2</sub> H . .	V.D.	12	14.0 ± 0.2	33	Trimer; $\Delta H_3^\circ$ 23
CF <sub>3</sub> ·CO <sub>2</sub> H . .	V.D.	20	14.0 ± 0.2	36	—

\* V.D. = vapour density.

†  $\Delta H^\circ$  in kcal. mole<sup>-1</sup>.

Before drawing conclusions from these figures we must consider the possible errors. Values of  $\Delta H_2^\circ$  obtained by the density-balance method<sup>12</sup> have a precision, it is claimed, of  $\pm 0.1$  kcal. mole<sup>-1</sup>, and those from the most recent version of the "classical" pressure-volume-temperature method a precision within  $\pm 0.2$  kcal. mole<sup>-1</sup>. Unfortunately the two methods do not agree within these limits; the respective values of  $\Delta H_2^\circ$  for acetic acid are  $15.27 \pm 0.1$  (Johnson and Nash) and  $13.8 \pm 0.2$  kcal. mole<sup>-1</sup> (Taylor). The discrepancy may be due to effects of adsorption which do not appear to have been taken into account in Taylor's experiments; or it may be due to the uncertainty in the calibration of the density balance. Errors in the entropy  $\Delta S_2^\circ$  are in general difficult to estimate; only for the most precise work, such as that just mentioned, are they as low as 0.2 cal. deg.<sup>-1</sup> mole<sup>-1</sup>, and most of the values cited are probably uncertain to the extent of at least 1 unit. The accuracy attained by any method depends on the temperature range covered, and the high values obtained by MacDougall for acetic<sup>14</sup> and propionic acid<sup>17</sup> may be due to the restricted range used by him (Table 1). The spectroscopic values of  $\Delta H_2^\circ$  are in reasonable agreement with the values from vapour-density methods, when it is remembered that the experimental error is of the order of 1 kcal. mole<sup>-1</sup> for the former. Some discrepancy might be expected, since the two methods will be differently affected by the presence of higher polymers and by deviations from the ideal gas laws. It is evident that, if the factors affecting dimerisation in the gas phase are to be elucidated, more extended series of acids should be investigated by precise methods under comparable conditions, and the discrepancies between the two vapour-density methods should be resolved.

When the uncertainties in the results are borne in mind, the following comments on the values of  $\Delta H_2^\circ$  may be made. The heats of dissociation of the carboxylic acid dimers are all in the region of  $14 \pm 1$  kcal. mole<sup>-1</sup> in the vapour phase. This is much less than would be expected for the breaking of a normal covalent bond, but is of the order of magnitude to be expected for a hydrogen bond if this is due mainly to electrostatic forces (cf. below). Neither the length of the hydrocarbon chain nor chain-branching has any great effect on the heat of dissociation, as was shown by Nash and his co-workers<sup>12, 18</sup> in the series acetic, propionic, heptanoic, and trimethylacetic acid. Electronegative substituents do not greatly alter  $\Delta H_2^\circ$ , if trifluoroacetic and acetic acid are typical; the range of substituted acids so far studied is not very extensive.

The standard entropy changes  $\Delta S_2^\circ$  are remarkably constant at about 35 units (apart from MacDougall's results) and there is again no marked dependence on the dimensions of the hydrocarbon chain. When a dimer dissociates into two monomeric molecules, the increase in entropy will be due mainly to the increase in the number of free particles, which gives rise to three extra translational degrees of freedom per molecule, with a smaller contribution from the extra degrees of rotational freedom. These factors would, according to ordinary statistical theory, lead to an increase of entropy in the region of 35 units, plus a contribution of a few units from



the freeing of rotation about the C-O bond (which will be restricted in the dimer). This result is in fair agreement with the experimental value. The order of magnitude of  $\Delta S_2^\circ$  and its approximate constancy can thus be understood in general terms. The detailed consideration of a particular acid is more complex, because in the dimer molecule the monomer units will not be rigidly fixed and the bonds between them will allow several kinds of bending and stretching motions. Given really accurate values of the entropies, we should be able to draw conclusions about the variation of the force constants of these bonds with the structure of the acid. Calculations on formic and acetic acid<sup>22</sup> suggest that values for the entropies are not in general reliable enough to permit this. However, it is possible to deduce a rough value for the force constant for symmetrical stretching of the hydrogen bonds in formic acid, namely  $3 (\pm 1.3) \times 10^4$  dynes per cm., and a value in this region is supported by some spectroscopic evidence.<sup>5b</sup> This would contribute about 2 units to the entropy. It is much smaller than the values for ordinary covalent X-H bonds, which are in the region of  $6 \times 10^5$  dynes per cm.

*Effect of substituents on equilibrium constant.* The equilibrium constant at a given temperature can be determined more accurately than either  $\Delta H_2^\circ$  or  $\Delta S_2^\circ$ , which depend on its variation with temperature. Thus a comparison of the values of  $K_2$  at one temperature is a more precise indication of the effects of the group R on the dimerisation of R-CO<sub>2</sub>H, though to interpret these effects we usually have to consider the heat and entropy of dimerisation, which both affect  $K_2$ .

Direct comparison of experimental values of  $K_2$  at one temperature is often not possible, because of the variety of conditions used (Table 1). However, for several acids values of  $K_2$  can be obtained at 160°, directly or by short extrapolations; the agreement between the results of different workers is better than for  $\Delta H_2^\circ$ . The results are collected in Table 3.

TABLE 3. *Equilibrium constants  $K_2$  for dissociation of dimers aliphatic acids in the vapour phase at 160°*

Acid	Ref.	$K_2$ (atm) at 160° in gas	$10^5 K_a$ at 25° in H <sub>2</sub> O (mole l <sup>-1</sup> )
CF <sub>3</sub> ·CO <sub>2</sub> H . . . . .	20	7.4	Strong
H·CO <sub>2</sub> H . . . . .	9, 20, 21	5.5*	17.7
Me·CO <sub>2</sub> H . . . . .	11, 10, 20	1.8†	1.76
Et·CO <sub>2</sub> H . . . . .	21	1.3	1.35
Pr·CO <sub>2</sub> H . . . . .	20	1.6	1.48
<i>n</i> -C <sub>6</sub> H <sub>13</sub> ·CO <sub>2</sub> H . . . . .	20	1.65	1.4
CMe <sub>3</sub> ·CO <sub>2</sub> H . . . . .	20	1.1	0.94

\* Individual values are 5.5 (Coolidge<sup>9</sup>), 5.5 (Nash<sup>20</sup>), and 5.6 (Taylor<sup>21</sup>).

† Individual values are 1.8 (Nash<sup>20</sup>), 2.1 (Taylor<sup>11</sup>), and 1.6 (Ritter and Simons<sup>10</sup>).

The value of  $K_2$  for the dissociation of the dimer (R-CO<sub>2</sub>H)<sub>2</sub> is seen to be little affected by the group R so long as this is a hydrocarbon group,

<sup>22</sup> Halford, *J. Chem. Physics*, 1946, **14**, 395.

but replacement by H or by  $\text{CF}_3$  increases  $K_2$  considerably. The figures for  $K_2$  are in the same order as the values of the acid dissociation constant in water at  $25^\circ$  which for these acids reflect the inductive effect of the group R. (In solution the results are roughly parallel; see below.)

The much larger dissociation of the formic and trifluoroacetic acid dimers might be due either to a lower heat of dissociation or to a larger entropy change on dissociation, corresponding to a stiffer bond in the dimer. Hence we need to consider the values of  $\Delta H_2^\circ$  and  $\Delta S_2^\circ$ . Unfortunately the results of different workers are not in agreement. Nash and his co-workers report that trifluoroacetic, formic, acetic, butyric, and trimethylacetic acid all have  $\Delta H_2^\circ = 14.0 (\pm 0.3)$  kcal. mole $^{-1}$  (Table 2), whereas a decrease of about 1.4 kcal. mole $^{-1}$  is required to account for the considerably larger dissociation constants of the first two acids in terms of  $\Delta H_2^\circ$ . They conclude that an explanation in terms of the heat of dissociation of the hydrogen bond is not admissible. However, Taylor's results indicate just such a decrease for formic acid (14.1 kcal. mole $^{-1}$  compared with 15.3 and 15.2 for acetic and propionic acid respectively). The question thus remains open from the experimental standpoint. It is indeed difficult to account for the greater dissociation of the dimers of the two strongest acids in terms of entropy changes; Lundin, Harris, and Nash<sup>20</sup> have been unable to do so from a consideration of the effects of the masses and dimensions of the substituents on the translational and rotational contributions to the entropy.

*Theoretical calculations of the heat of dimerisation.* If it is true that the hydrogen bonds in the dimer are predominantly electrostatic, it should be possible to show that calculations of the heat of dimerisation  $\Delta H_2^\circ$  based on electrostatic interaction agree with the experimental values. This is certainly verified as regards order of magnitude, as is shown by a variety of calculations on the formic acid dimer. (Strictly, such calculations yield values of the contribution of molecular interactions to the standard free energy change,  $\Delta G_2^\circ$ , without regard to thermal motion, *i.e.*, at absolute zero where  $\Delta G_2^\circ$  can be identified with the corresponding internal energy of dimerisation,  $\Delta U_2^\circ$ . At finite temperatures the identification is an approximation.  $\Delta U_2^\circ$  is related to  $\Delta H_2^\circ$  by the equation  $\Delta H_2^\circ = \Delta U_2^\circ + P\Delta V$  ( $P$  = pressure;  $V$  = volume); since each mole of dimer gives rise to two moles of monomer,  $P\Delta V = RT$ , and so, with  $T$  in the region of  $400^\circ \text{K}$ , about 800 cal. per mole must be added to  $\Delta V_2^\circ$  in order to obtain  $\Delta H_2^\circ$ ).

A simple calculation taking account only of the interaction of the permanent dipoles of the hydroxyl and the carboxyl group (assumed to be the same as in other compounds) gives a value of  $\Delta H_2^\circ$  in the region of 12 kcal. mole $^{-1}$ .<sup>23</sup> In a later treatment<sup>24</sup> the induced dipoles were also taken into consideration and the permanent dipoles were treated by resolution into point charges at appropriate distances (taken from Pauling and Brockway's results) so that allowance could be made for all the interactions.<sup>24</sup> This gave  $\Delta H_2^\circ = 14.2$  kcal. mole $^{-1}$ , made up of 11.2 kcal. from simple dipole interaction, 2.2 kcal. from induced dipole interaction, and 0.8 kcal.

<sup>23</sup> Moelwyn-Hughes, *J.*, 1938, 1243.

<sup>24</sup> M. M. Davies, *Trans. Faraday Soc.*, 1940, **36**, 341.

from  $P\Delta V$ . The agreement with the experimental value of  $14.1 \pm 0.1$  kcal. mole<sup>-1</sup> might appear very satisfactory ; but dispersion forces and repulsion forces have been neglected, and contributions from these, though probably minor and of opposite sign, cannot be reliably estimated. A calculation taking into account the attractive forces of dispersion gives  $\Delta H_2^0 = 16.7$  kcal. mole<sup>-1</sup>, while a calculation in which repulsive forces also are considered <sup>25</sup> gives  $\Delta H_2^0 = 11.0$  kcal. mole<sup>-1</sup> (on Karle and Brockway's model <sup>1</sup>). The two values lie on either side of that calculated from electrostatic forces alone, and differ appreciably from it. The difficulties associated with intermolecular forces at short distances thus prevent a precise confirmation of the view that the bonds are mainly electrostatic, though there is no doubt that this view gives a good approximation to the true value of  $\Delta H_2^0$ .

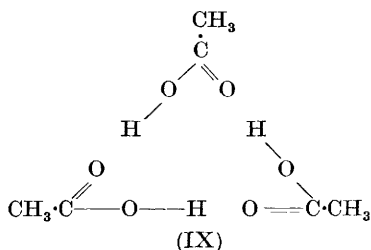
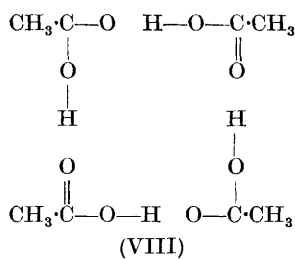
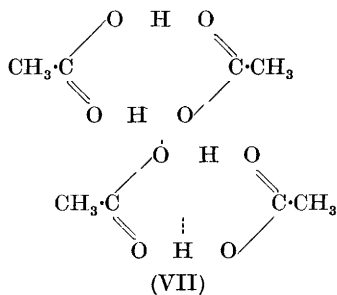
Such calculations start from the empirical values of the distances and dipole moments concerned. Quantum-mechanical calculations which assume only the ring structure of the dimer and lead to estimates of both energies and bond length have been attempted by Gillette and Sherman,<sup>26</sup> using the resonance method. They obtained a value for  $\Delta H_2^0$  on the assumption that the structures (I) and (II) participate, and another on the assumption that twelve other possible non-ionic structures are also involved. Neither value was in reasonable agreement with experiment. Gillette and Sherman concluded that ionic canonical forces must be included in the calculation and, as we have noted, these appear from later calculations to contribute most of the energy <sup>2</sup>; but explicit calculations of  $\Delta H_2^0$  based on them seem not to have been reported.

**Higher Polymers.**—Several workers have found that dimerisation alone does not account for their observations, and the deviations have usually been ascribed either to the formation of higher polymers of the acids, or to non-ideal behaviour of the mixture of gases. It is, however, very difficult to distinguish between deviations of a vapour from ideality and the association of its molecules, since both depend on intermolecular forces. Johnson and Nash <sup>12</sup> used a quantitative method of differentiating between them. The experimental results were subjected to two forms of analysis. In the first the gaseous imperfections were estimated on the assumption that no higher polymers were present. In the second, the possibility of polymers higher than the dimer was considered, on the assumption that the gaseous mixture was ideal. Only the second analysis gave satisfactory results ; the first gave highly improbable values for the second virial coefficients of the monomer and dimer. Most workers have considered only one or other of the two possibilities. Thus Coolidge <sup>9</sup> assumed that the deviations shown by formic acid were due to non-ideal behaviour of the monomeric and the dimeric species, and obtained a satisfactory correlation of his experimental data without considering higher polymers. MacDougall <sup>17</sup> found that even at low pressures the equilibrium constants calculated for the dimerisation of propionic acid increased with pressure. This was attributed to the existence

<sup>25</sup> Jones, Gilkerson, and Gallup, *J. Chem. Phys.*, 1952, **20**, 1048 ; Maladière, *Compt. rend.*, 1948, **226**, 1600.

<sup>26</sup> Gillette and Sherman, *J. Amer. Chem. Soc.*, 1936, **58**, 1135.

of a trimer, and the heat of trimerisation was calculated and found to be about 1.5 times the heat of dimerisation, which suggested that the hydrogen bonds in the trimer were comparable in strength with those in the dimer. Ritter and Simons<sup>10</sup> found that non-ideal behaviour could not account for their observations on the association of acetic acid vapour. They considered a monomer-trimer equilibrium, but rejected it in favour of an equilibrium between monomeric, dimeric and tetrameric species, which fitted their experimental data better. They proposed a layer structure (VII) for the tetramer, in preference to a ring structure (VIII), on the ground that the ring would be strained and could only be formed by breaking exothermic bonds; the same arguments suggested that the trimer (IX) should be less stable than the tetramer. The heat of dissociation calculated for the tetramer was about twice that of the dimer, suggesting strong hydrogen bonds between the layers. Ritter and Simons assumed that in the hydrogen bonds the hydrogen atoms were symmetrically placed between the oxygen atoms; the layer structure would be less regular when rewritten to conform with later information on the O-H distances.<sup>1</sup>



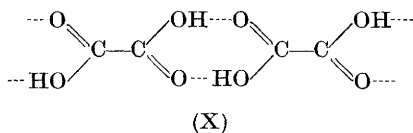
The most thorough investigation of higher polymers is due to Johnson and Nash.<sup>12</sup> The equilibrium constants for the dimerisation of acetic, trimethylacetic, and butyric acid, when calculated from the vapour density on the assumption that no higher polymers were present, showed a pronounced variation with density. The experimental results, when analysed as mentioned above, indicated the presence of higher polymers, notably a trimer; the presence of a tetramer was considered to be doubtful. The strengths of the hydrogen bonds in the trimer (calculated from its heat of dissociation) were again of the same order as the bonds in the dimer. There is some uncertainty in the evaluation of the standard entropy change for

trimerisation, which depends on the choice of the equation of state of the standard substance (carbon tetrachloride). Johnson and Nash have also subjected the results obtained by Coolidge<sup>9</sup> for formic acid to the same analysis, and found rather tenuous evidence for the presence of a trimer with a heat of dissociation  $\Delta H_3^0 = 16$  kcal. mole<sup>-1</sup>. The fact that  $\Delta H_3^0$  was here little more than the heat of dissociation of the dimer (14 kcal. mole<sup>-1</sup>) was interpreted to mean that the aggregate was not, like the dimer, a stable species, and might only be a transient collision complex. Johnson and Nash also discussed the structure of the trimer; and concluded that the most likely was a non-planar 12-membered ring.

It should be noted that in three of these investigations the experiments were conducted at relatively high pressures, and that in two investigations of acetic acid at lower pressures no higher polymerisation was observed. The higher polymers would be formed in greater proportion as the pressure increased; but the deviations from ideality must also increase, and this makes the evidence for the presence of higher polymers less convincing. There appears to be a need for an investigation extending over a range of pressures from, say, 2 to 400 mm., to elucidate the conditions under which higher polymers are formed.

### III. Hydrogen Bonding in Solid Carboxylic Acids

Evidence on hydrogen bonding in the solid state is much less extensive than for the vapour state. Early X-ray investigations<sup>27</sup> on solid fatty acids indicated that the hydrocarbon chains lie parallel to one another and are associated in collinear pairs, presumably with the carboxyl groups together. This arrangement persists in the melt. Later work has been mainly concerned with dicarboxylic acids. Oxalic acid crystallises in two forms,  $\alpha$  and  $\beta$ , in both of which certain of the O—H—O distances are so short that they indicate hydrogen bonds.<sup>28</sup>  $\beta$ -Oxalic acid exhibits the cyclic structure found in formic acid vapour; the molecules are linked end to end in infinite chains, represented by (X). (The forces between the chains are comparatively weak, as indicated by the O—O distances.)

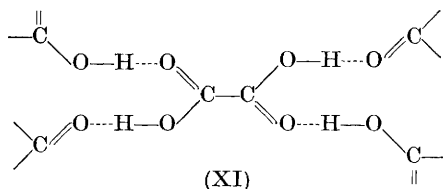


A similar structure is found in the  $\beta$ -form of succinic acid and in the higher members of the dicarboxylic acid series. In  $\alpha$ -oxalic acid, the hydrogen bonds link the molecules into puckered sheets (XI); the O—O distance in the grouping C=O $\cdots$ HO—C is 2.71 Å, short enough to indicate clearly a hydrogen bond.

<sup>27</sup> Muller, *J.*, 1923, 2043, 3156; Morrow, *Phys. Review*, 1928, **31**, 10.

<sup>28</sup> (a) Hendricks, *Z. Kryst.*, 1935, **91**, 48; (b) Cox, Dougill, and Jeffrey, *J.*, 1952, 4854; (c) Ahmed and Cruickshank, *Acta Cryst.*, 1953, **6**, 385.

It would be expected that hydrogen bonding would be responsible for most of the lattice energy of each of these structures. There are two hydrogen bonds per molecule of oxalic acid, and, if the heat of dissociation of each bond has about the value found for monocarboxylic acids in the gas phase, the lattice energy will be in the region of 14 kcal. mole<sup>-1</sup>. The



values estimated by Bradley and Cotson<sup>29</sup> from vapour-pressure measurements are 22.3 kcal. for the  $\beta$ - and 23.4 kcal. for the  $\alpha$ -form. These are of the right order of magnitude for hydrogen bonds, and it must be remembered that the uncertainty in estimating the dispersion and the repulsion energy, as well as the electrostatic energy, is even greater in the solid than in the gaseous state, because of the effects of the non-nearest neighbours.

Solid formic acid, according to recent preliminary results, has a crystal structure that precludes the possibility of dimers in the solid and suggests that the molecules are arranged in infinite chains in which each molecule is linked to two neighbours by hydrogen bonds.<sup>30</sup>

#### IV. Association in Solution

**Structure of the Dimer.**—Results obtained by a variety of methods, discussed below, show that carboxylic acids are associated in hydrocarbons and similar solvents, and that in dilute solutions the associated molecule is dimeric. There is no such direct evidence that the dimer is cyclic in solution as there is for the gas phase, but from the parallelism of the results there is little reason to doubt it. There is direct evidence, from Davies and Sutherland's work on the infra-red spectra of formic and acetic acids in carbon tetrachloride,<sup>6</sup> that the O—H bond of the carboxyl group is slightly longer in the dimer than in the monomer, that the hydrogen is not symmetrically placed, and that the C—O bonds are not all equal in length. The bond lengths (Å) found for the formic acid monomer and dimer are :

	O—H	C=O	C—O
Monomer	0.9 <sub>8</sub>	1.1 <sub>9</sub>	1.3 <sub>0</sub>
Dimer	1.0 <sub>4</sub>	1.2	1.2 <sub>9</sub>

The fact that the O—H distance is only slightly greater in the dimer accords with an interpretation of the association in terms of a looser interaction than covalency. The bearing of the results on the question of the canonical forms involved in resonance has been mentioned on p. 256.

**Experimental Work on the Equilibrium in Solution.**—The tendency to associate is measured, as in the gas phase, by the equilibrium constant.

<sup>29</sup> Bradley and Cleasby, *J.*, 1953, 1681; cf. Bradley and Cotson, *J.*, 1953, 1684.

<sup>30</sup> Holtzberg, Post, and Fankuchen, *J. Chem. Phys.*, 1952, **20**, 198.

Most workers have used dilute solutions, so that thermodynamic activities may be replaced by concentrations, which are conveniently expressed as mole fractions; thus if the mole fraction of monomer is  $x_1$  and of dimer  $x_2$ ,  $K_2 = x_1^2/x_2$ . Values of  $\Delta G_2^\circ$ ,  $\Delta H_2^\circ$ , and  $\Delta S_2^\circ$  can then be derived from  $K_2$  as above.

The value of  $K_2$  in solution is sometimes expressed in moles per l. Concentrations expressed in these units show a temperature-variation due to thermal expansion of the solution; thus  $K_2$  will vary with the density of the solution, as well as with the displacement of equilibrium; and the temperature-dependence of  $K_2$  will lead to values of  $\Delta H_2^\circ$  slightly different from those derived from  $K_2$  in terms of mole fractions. In practice the error is only 2–3% for benzene solutions, for example, if the temperature range is about 30°.

A difficulty arises about units when comparisons have to be made with the gas phase. Only when the values of  $K_2$  in the gas phase and in solution are expressed in the same units will the standard entropies derived therefrom relate to the same standard state. For the gas phase, we have expressed  $K_2$  in atm.; since one l. of gas at 25° contains about 0.041 mole, the unit of concentration at 25° is 0.041 mole per l. For solutions we must adopt the same concentration scale whenever we make comparisons with the gas phase. For benzene, 1 l. of liquid contains about 11.3 moles, so a solution of mole fraction  $x$  contains 11.3 $x$  moles and its concentration expressed in the units used for the gas phase is (11.3/0.041) $x$ . Since we calculate  $\Delta S_2^\circ$  from the equation  $\Delta S_2^\circ = \Delta H_2^\circ/T + R \ln K_2$  the adoption of this unit requires us to add  $R \ln (11.3/0.041)$  or about 11 cal. deg.<sup>-1</sup> mole<sup>-1</sup> to the value of  $\Delta S_2^\circ$  calculated from  $K_2$  in mole fraction units. This is important (see p. 272).

The range of acids studied in solution is greater than that in the gas phase—aromatic and unsaturated aliphatic acids have been studied, as well as fatty acids—but the precision is somewhat lower.

*Earlier work indicating dimerisation in aprotic solvents.* Early investigations produced good evidence that carboxylic acids are partly or completely dimerised in solvents such as benzene or carbon tetrachloride. The existence of double molecules was inferred by Beckmann<sup>31</sup> in 1890 from his determinations of the molecular weights of carboxylic acids in organic solvents by the depression of freezing-point. Nernst<sup>32</sup> in 1891 explained the distribution of benzoic acid between water and an inorganic solvent in terms of dimerisation in the organic solvent. By studying the distribution of acid between water and benzene or chloroform, Hendrixson<sup>33</sup> in 1897 determined the equilibrium constant for dimerisation at two temperatures and thence calculated the heat of dissociation of the dimer. Some cryoscopic work by Trautz and Moschel<sup>34</sup> in 1926 suggested that polymers higher than the dimer were present in solutions of acetic acid in

<sup>31</sup> Beckmann, *Z. physikal. Chem.*, 1890, **6**, 444.

<sup>32</sup> Nernst, *ibid.*, 1891, **8**, 110.

<sup>33</sup> Hendrixson, *Z. anorg. Chem.*, 1897, **13**, 73.

<sup>34</sup> Trautz and Moschel, *ibid.*, 1926, **155**, 13.

benzene or nitrobenzene; this has not been observed in later work with dilute solutions. In the same year Brown and Bury<sup>35</sup> reported cryoscopic measurements, by the Beckmann method, for several carboxylic acids in nitrobenzene; their results were complicated by deviations from ideal behaviour, but when later reinterpreted by Wynne-Jones and Rushbrooke<sup>36</sup> gave evidence for a dimerisation equilibrium; it was found that addition of water decreased the apparent degree of association. Cryoscopic measurements were also carried out by Peterson and Rodebush,<sup>37</sup> who used the much superior method due originally to Adams,<sup>38</sup> in which equilibrium is assured by using an intimate mixture of solution and crushed solid solvent, the concentration being estimated after withdrawal of a sample of the equilibrated solution; further, the freezing-point depression is directly and accurately measured by means of a multi-junction thermocouple with one set of junctions in the mixture of solution and solid solvent and the other in a mixture of solid and liquid solvent. With benzene as solvent, it was possible to cover a range of concentrations in which the apparent molecular weight of acetic acid varied from nearly the single value to nearly the double value; that of benzoic acid varied much less over the same range. Evidence that at higher temperatures dimerisation is incomplete in benzene for a variety of acids, and depends upon structure, appears to have been first provided by Brocklesby,<sup>39</sup> who determined the boiling-point elevations of solutions in benzene, and other solvents, by a method accurate to about 0.01°; he found that at about 80° the degree of association in benzene varies with concentration, and that in a series of fatty acids at a fixed concentration it decreases up to dodecanoic acid, after which it remains almost constant. Trichloroacetic acid and its hydrate were studied cryoscopically in benzene by Bell and Arnold,<sup>40</sup> who found that the anhydrous acid formed double molecules, while the hydrate was present as single molecules in dilute solution.

It was thus established that dimerisation equilibria were set up, that the equilibrium could be measured at reasonable temperatures, and that it varied from acid to acid. It was also shown that the equilibrium was affected by the presence of water. Little was known, however, about the values of the equilibrium constants or their variation with temperature. Since about 1945, these have been investigated increasingly by a variety of methods. Aprotic solvents have generally been used; work in other solvents is briefly noticed at the end of the section.

*Determination of equilibrium constants for dimerisation in solution.* The methods that have been used include use of cryoscopy, vapour-pressure measurements, ebullioscopy, dielectric constants, absorption spectroscopy, and distribution measurements. Of these, freezing-point measurements offer high precision and have been used by Barton and Kraus,<sup>41</sup> but are applicable

<sup>35</sup> Brown and Bury, *J. Phys. Chem.*, 1926, **30**, 694.

<sup>36</sup> Wynne-Jones and Rushbrooke, *Trans. Faraday Soc.*, 1944, **40**, 345.

<sup>37</sup> Peterson and Rodebush, *J. Phys. Chem.*, 1928, **32**, 709.

<sup>38</sup> Adams, *J. Amer. Chem. Soc.*, 1915, **37**, 481.

<sup>39</sup> Brocklesby, *Canad. J. Res.*, 1936, **14**, B, 222.

<sup>40</sup> Bell and Arnold, *J.*, 1935, 1432.

<sup>41</sup> Barton and Kraus, *J. Amer. Chem. Soc.*, 1951, **73** 4561.



only at one temperature. The ebullioscopic method give results of lower precision, and cannot be applied if the acid is too volatile ; but as the boiling temperature can be varied, by altering the pressure, the equilibrium constant can be measured over a range of temperature and the heat and entropy of dimerisation determined,<sup>42, 43</sup> though less accurately than for the best gas-phase determinations. This holds also for the vapour-pressure method, which has been applied by Wall and Baner ;<sup>44</sup> they used an isopiestic method and obtained an accuracy of the same order as that of ebullioscopic measurements in determining heats of dimerisation. Dielectric constants of solutions of many carboxylic acids in benzene have been measured at one temperature by Hobbs and Gross,<sup>45</sup> who fitted the results in dilute solution to an equation for a dimerisation equilibrium and evaluated the equilibrium constant ; the precision of this method is difficult to assess, but is certainly not high. A spectroscopic investigation of solutions of acetic acid in carbon tetrachloride was carried out by Davies and Sutherland,<sup>6</sup> who measured the intensity of the absorption band of the hydroxyl group over a range of concentrations at three temperatures, and obtained a reasonable value for  $\Delta H_2^0$  ; the results for benzoic acid were, however, rather erratic. The distribution of acetic and propionic acid between water and various aprotic

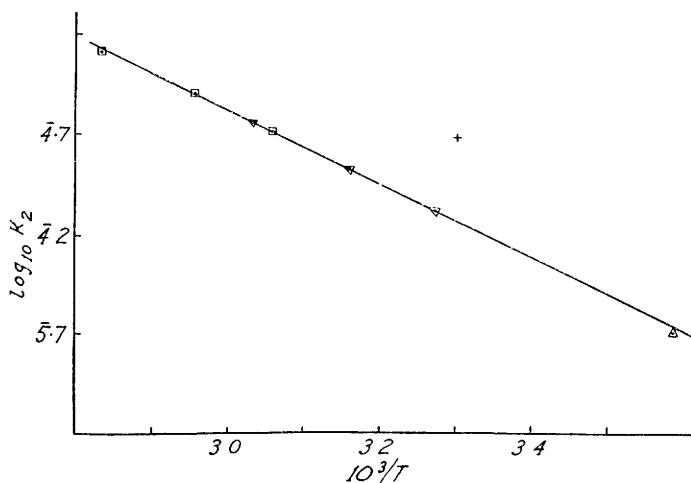


FIG. 1

Dissociation of benzoic acid dimers in benzene, as a function of temperature : plot of  $\log_{10} K_2$  against  $1/T$ .

- △ Freezing-point depression method.<sup>41</sup>
- Vapour-pressure depression method.<sup>44</sup>
- Boiling-point elevation method.<sup>43</sup>
- + Dielectric-constant method.<sup>45</sup>

<sup>42</sup> Wolf and Metzger, *Annalen*, 1949, **563**, 157.

<sup>43</sup> Allen and Caldin, *Trans. Faraday Soc.*, in the press.

<sup>44</sup> Wall and Baner, *J. Amer. Chem. Soc.*, 1945, **67**, 898.

<sup>45</sup> Hobbs and Gross, *J. Chem. Phys.*, 1941, **9**, 408, 415 ; *J. Amer. Chem. Soc.*, 1949, **71**, 1671.

solvents has been studied at a series of temperatures, and values of the heats and entropies of dimerisation deduced; <sup>46</sup> this method requires a comparatively simple technique, the temperature can be varied, and solutions in various solvents can be compared at a fixed temperature; but there is some uncertainty about the effects of the water dissolved in the organic solvent.

The mutual agreement of results obtained by the first three methods in their different temperature-ranges can be seen from Fig. 1, in which values of  $\log_{10} K_2$  are plotted against  $1/T$ . The agreement is evidently satisfactory. The mean value of  $\Delta H_2^\circ$ , the heat of dissociation of the dimer, over the range  $5^\circ$ — $80^\circ\text{C}$ ., can be determined as  $8.4 \pm 0.5$  kcal. mole<sup>-1</sup>. Comparisons between these three results and the others mentioned may be made with the aid of Table 6. The dielectric-constant method gives results that agree fairly well with those from vapour-pressure measurements for *m*- and *o*-toluic acid, but not for benzoic acid. For acetic and propionic acid, the dielectric-constant results do not agree with those from distribution experiments, and here it is more difficult to decide which are the more reliable; for the series of substituted fatty acids the dielectric-constant results will be used as giving a series of comparative values.

*Heats and entropies of dissociation of dimeric carboxylic acid molecules in benzene solution.* The heats and standard entropies of dissociation of carboxylic acid dimers in benzene (the solvent most commonly used) have

TABLE 4. *Standard free energies, heats, and entropies of dissociation of dimers of carboxylic acids in benzene, at 25°.*

Calc. from  $K_2$  in mole fraction units.

Acid	Ref.	Method	$\Delta G_2^\circ$ at 25° (kcal. mole <sup>-1</sup> )	$\Delta H_2^\circ$ (kcal. mole <sup>-1</sup> )	$\Delta S_2^\circ$ (cal. deg. <sup>-1</sup> mole <sup>-1</sup> )	$T\Delta S_2^\circ$ at 25° (kcal. mole <sup>-1</sup> )
BzOH . . . .	33	Distn.	—	8.7	—	—
„ . . . .	43	B.p.	$5.18_5 \pm 0.06$	$8.0_4 \pm 0.4$	$9.6 \pm 1.5$	$2.8_5 \pm 0.4$
„ . . . .	44	V.p.	$5.26 \pm 0.04$	$8.4 \pm 0.2$	$10.6 \pm 1.5$	$3.1_5 \pm 0.2$
„ . . . .	42	B.p. & f.p.	—	10.5	—	—
<i>o</i> -C <sub>6</sub> H <sub>4</sub> Me·CO <sub>2</sub> H .	44	V.p.	$5.03 \pm 0.04$	$8.4 \pm 0.2$	$11.3 \pm 1.5$	$3.4 \pm 0.2$
<i>m</i> -C <sub>6</sub> H <sub>4</sub> Me·CO <sub>2</sub> H .	44	V.p.	$5.44 \pm 0.05$	$9.4_4 \pm 0.2$	$13.4 \pm 1.5$	$4.0 \pm 0.2$
<i>p</i> -C <sub>6</sub> H <sub>4</sub> Me·CO <sub>2</sub> H .	43	B.p.	$6.05 \pm 0.06$	$8.7_5 \pm 0.4$	$10.1 \pm 1.6$	$3.0 \pm 0.4$
<i>p</i> -MeO·C <sub>6</sub> H <sub>4</sub> ·CO <sub>2</sub> H	43	B.p.	$5.17 \pm 0.06$	$8.7_5 \pm 0.4$	$12.0 \pm 1.5$	$3.6 \pm 0.4$
<i>m</i> -C <sub>6</sub> H <sub>4</sub> I·CO <sub>2</sub> H .	43	B.p.	$4.99 \pm 0.08$	$7.8_8 \pm 0.5$	$9.7 \pm 1.5$	$2.9 \pm 0.6$
<i>o</i> -C <sub>6</sub> H <sub>4</sub> Cl·CO <sub>2</sub> H .	43	B.p.	$4.74 \pm 0.05$	$8.6 \pm 0.3$	$13.0 \pm 1.4$	$3.8_5 \pm 0.4$
Ph·C <sub>6</sub> H <sub>4</sub> ·CO <sub>2</sub> H . .	43	B.p.	$4.10 \pm 0.05$	$9.1 \pm 0.4$	$16.8 \pm 1.4$	$5.0 \pm 0.4$
Me·CO <sub>2</sub> H . . . .	46	Distn.	$4.3 \pm 0.1^*$	$8.2 \pm 0.7$	$13.0 \pm 2^*$	$3.9 \pm 0.7$
Et·CO <sub>2</sub> H . . . .	46	Distn.	$4.3 \pm 0.1^*$	$7.8 \pm 0.6$	$11.5 \pm 2^*$	$3.4 \pm 0.6$

\* Recalc. after conversion of  $K_2$  into mole fraction units.

been collected into Table 4 from all the investigations of equilibrium constants in which the temperature has been varied. The heats of dissociation,

<sup>46</sup> (a) M. M. Davies, Jones, Patnaik, and Moelwyn-Hughes, *J.*, 1951, 1249. (b) The values for  $\Delta S_2^\circ$  in carbon disulphide and in nitrobenzene given in this paper have been replaced by values corrected in accordance with a personal communication from Dr. E. A. Moelwyn-Hughes.

$\Delta H_2^\circ$ , are mostly accurate to about  $\pm 0.4$  kcal. mole<sup>-1</sup>, and the standard entropies  $\Delta S_2^\circ$  to about  $\pm 1.5$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>, so that  $T\Delta S_2^\circ$  is known to about  $\pm 0.4$  kcal. mole<sup>-1</sup>. Values of  $\Delta G_2^\circ (= -RT \ln K_2)$  are given for reference; they are known much more accurately, to about  $\pm 0.06$  kcal. mole<sup>-1</sup>.

From the Table it appears that the heat-content change does not vary greatly from acid to acid, or between aliphatic and aromatic acids; it is in the region of 9 kcal. mole<sup>-1</sup>, compared with about 14 kcal. mole<sup>-1</sup> for aliphatic acids in the gas phase. The standard entropy change,  $\Delta S_2^\circ$ , is in the region of 11 units for nearly all the acids. To obtain  $\Delta S_2^\circ$  for the standard state corresponding to that adopted for the gas phase, we must add about 11 units (p. 269). The standard entropy change is then about 22 units, compared with about 35 units for aliphatic acids in the gas phase. Thus the hydrogen bonds require less energy for dissociation in benzene solution than in the vapour, but the effect of this in favouring monomer at the expense of dimer is offset by the smaller entropy change on dissociation, the changes in  $\Delta H_2^\circ$  and in  $T\Delta S_2^\circ$  being of comparable magnitude and opposite effect on  $K_2$  [ $\partial(\Delta G_2^\circ) = -\partial(RT \ln K_2) = \partial(\Delta H_2^\circ) - \partial(T\Delta S_2^\circ)$ ]. The smaller entropy and heat-content changes can be attributed to solvation, and confirm the view, for which there is other evidence, that benzene is, not an "inert", but a donor solvent. It is very probable that the monomers will be more solvated than the dimers, on account of the local dipoles of the hydroxyl and carboxyl groups, which are masked in the dimers; even the resultant dipole moment of the molecule as a whole is known to be higher for the monomers (*ca.* 1.8 D, compared with *ca.* 1.0 D for the dimer molecules<sup>45</sup>). The monomer thus has a greater power of polarising the solvent molecules and orientating them by dipole interaction. There is therefore a partial "freezing" of molecules round the monomer, which implies a gain of molecular order, and a consequent decrease of entropy which partly compensates for the increase due to the greater number of molecules. Solvation will also lower the energy of the monomer more than that of the dimer and so make  $\Delta H_2^\circ$  smaller than that in the gas phase. We might thus expect a correlation between  $\Delta H_2^\circ$  and  $\Delta S_2^\circ$ , and, as we shall see, some correlation is found on varying the solvent, whose polarity affects both quantities. There are also some signs of a correlation between  $\Delta H_2^\circ$  and  $\Delta S_2^\circ$  for the aromatic acids in Table 4, but this may be illusory since the changes are little greater than the experimental uncertainties.

*Solvent effects in aprotic solvents.* For a series of solvents without specific hydrogen-bonding properties, this explanation in terms of solvation would lead us to expect that the effects on  $\Delta H_2^\circ$  and  $\Delta S_2^\circ$  (compared with the vapour) would be greater the more polar and polarisable the molecules of the solvent. The only systematic results on a series of aprotic solvents, at several temperatures, are those obtained for acetic and propionic acid by Davies, Moelwyn-Hughes, *et al.*,<sup>46</sup> using the distribution method (*i.e.*, solvents saturated with water). Some of their results for acetic acid are given in Table 5. It will be seen that as the dielectric constant of the solvent (representing its polarity) increases,  $\Delta H_2^\circ$  and  $\Delta S_2^\circ$  decrease, with a roughly

linear relation between them. These results are evidently in accord with the above interpretation in terms of solvation of dipolar molecules.

TABLE 5. *Dissociation of dimeric acetic acid in various solvents*  
 $K_2$  in mole l.<sup>-1</sup> units

Solvent	Dielectric constant at 25°	$\Delta H_2^0$ (kcal mole <sup>-1</sup> )	$\Delta S_2^0$ (cal deg <sup>-1</sup> mole <sup>-1</sup> )	$10^3 K_2$ at 35°
Vapour . . . . .	1.00	14.5	28	0.07
C <sub>6</sub> H <sub>14</sub> . . . . .	1.87	9.0	17	1.9
C <sub>6</sub> H <sub>6</sub> . . . . .	2.25	8.2	18	12.4
CCl <sub>4</sub> . . . . .	2.22	7.6	13	3.1
CS <sub>2</sub> . . . . .	2.60	7.05	10.6	2.8
C <sub>6</sub> H <sub>5</sub> Cl . . . . .	6.37	5.0	7	9.4
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> . . . . .	33.1	5.25	13.6	180

A different, but ultimately equivalent, way of approaching the matter is the following. The energy when two dipoles approach each other can be calculated, on certain assumptions, and the effect of variation of the dielectric constant of the solvent on this free energy (and so on  $K_2$ ) can be derived. Now the dielectric constant depends on the ability of the solvent molecules to orient themselves in an electric field. But this property also determines their solvating properties in these solutions. Thus an explanation in terms of dielectric constant ( $\epsilon$ ) is equivalent to an explanation in terms of solvation. On the simplest assumptions,<sup>23, 46</sup> one finds that  $\log_{10} K_2$  should vary linearly with  $1/\epsilon$  and that  $\Delta H_2^0$  should be given by  $\Delta H_2^0 = [(1 - LT)/\epsilon]\Delta H_2^g$ , where  $\Delta H_2^g$  is the value in the gas phase and  $L = (de/dT)$ . The first of these relations is roughly obeyed;  $K_2$  increases with increase of dielectric constant (the effect on  $\Delta G_2^0$  of the decrease in  $\Delta H_2^0$  being greater than that of the decrease in  $\Delta S_2^0$ ), though the plot of  $\log_{10} K_2$  against  $1/\epsilon$  is somewhat scattered. The second relation is obeyed more accurately.<sup>46</sup> Although it is not at all clear that the assumptions involved are valid—particularly the assumption that the bulk dielectric constant is relevant to conditions near a solute molecule—it seems that the results so far available on variation of the solvent, though in need of support, are at least consistent with an electrostatic interpretation of the hydrogen bond.

**Structure of Acids and Dimerisation in Benzene.**—The view that hydrogen bonding in carboxylic acid dimers is largely due to dipole interaction would lead us to expect that it should depend on the inductive and mesomeric effects of substituents. These effects are also important in determining the strengths of the acids in water, so that at a fixed temperature we might expect some relation between the dissociation constants of dimeric acids in some aprotic solvent and the acid dissociation constant in water. Such relations have been reported for various limited series of acids, all in benzene solution, by several workers. Hobbs and Gross,<sup>45</sup> from their measurements of dielectric constants, conclude that there is a rough parallelism between the dissociation equilibrium constant,  $K_2$ , for the dimers in benzene

(measured at 30°) and the acid dissociation  $K_a$  in water (at 25°); in the lower fatty acids, an electronegative substituent increases the degree of dissociation of the dimer while an electropositive group decreases it. Barton and Kraus<sup>41</sup> from their more precise freezing-point work found that four acids—benzoic, *o*-bromobenzoic, phenylpropionic, and cinnamic—gave a roughly linear relation between  $\log_{10} K_2$  (at 5.5°) and  $\log_{10} K_a$  (at 25°), from which, however,  $\beta$ -phenylpropionic acid deviated considerably. Wall and Banes's vapour-pressure data<sup>44</sup> show a nearly linear logarithmic relation at 25° for benzoic, *m*-toluic, and *o*-toluic acid, and this has been found to cover also *o*-chlorobenzoic, *m*-iodobenzoic, and phenylpropionic acid, the points for *p*-toluic and *p*-anisic acid deviating somewhat from the line.<sup>43</sup>

Table 6 shows the data on twenty-one acids for which the constant  $K_2$  is known at 30°, either directly or by extrapolation from measurements over a range of temperatures. Not all of the acid dissociation constants,  $K_a$ , are known at 30°, so we have used the values at 25° (where the values of  $\log_{10} K_a$  at 30° are known, they do not differ by more than 0.05 from those at 25°).

TABLE 6. *Dissociation of dimers in benzene at 30° and acid dissociation in water at 25°*

$K_2$  in mole fraction units;  $K_a$  in mole l.<sup>-1</sup> units.

No. in Fig. 2	Acid	Ref.	5 + $\log_{10} K_2$ at 30°	6 + $\log_{10} K_a$ at 25°
1	<i>p</i> -C <sub>6</sub> H <sub>4</sub> Me·CO <sub>2</sub> H . . . . .	43	0.68 ± 0.04	1.637
2	<i>m</i> -C <sub>6</sub> H <sub>4</sub> Me·CO <sub>2</sub> H . . . . .	44	1.20 <sub>5</sub> ± 0.04	1.726
		45	1.25	
3	BzOH " . . . . .	43	1.29 <sub>5</sub> ± 0.04	1.820
	" . . . . .	44	1.27 ± 0.04	
	" . . . . .	45	1.68	
4	<i>p</i> -MeO·C <sub>6</sub> H <sub>4</sub> ·CO <sub>2</sub> H . . . . .	43	1.31 ± 0.04	1.529
5	<i>o</i> -C <sub>6</sub> H <sub>4</sub> Me·CO <sub>2</sub> H . . . . .	44	1.43 ± 0.04	2.086
	" . . . . .	45	1.34	
6	<i>m</i> -C <sub>6</sub> H <sub>4</sub> I·CO <sub>2</sub> H . . . . .	43	1.43 ± 0.05	2.150
7	<i>o</i> -C <sub>6</sub> H <sub>4</sub> Cl·CO <sub>2</sub> H . . . . .	43	1.63 ± 0.04	3.079
8	<i>o</i> -C <sub>6</sub> H <sub>4</sub> F·CO <sub>2</sub> H . . . . .	45	1.67	2.73
9	<i>m</i> -C <sub>6</sub> H <sub>4</sub> F·CO <sub>2</sub> H . . . . .	45	0.70	2.13
10	<i>p</i> -C <sub>6</sub> H <sub>4</sub> F·CO <sub>2</sub> H . . . . .	45	0.85	1.86
11	CMe <sub>3</sub> ·CO <sub>2</sub> H . . . . .	45	1.12	0.973
12	Pr <sup>n</sup> ·CO <sub>2</sub> H . . . . .	45	1.32	1.176
13	Et·CO <sub>2</sub> H . . . . .	46	1.92	1.130
	" . . . . .	45	1.36	
14	Me·CO <sub>2</sub> H . . . . .	46	1.89	1.246
	" . . . . .	45	1.38	
15	CH <sub>3</sub> Ph·CO <sub>2</sub> H . . . . .	45	1.42	1.69
16	CH <sub>2</sub> Ph·CH <sub>2</sub> ·CO <sub>2</sub> H . . . . .	45	1.43	1.34
17	H·CO <sub>2</sub> H . . . . .	45	1.85	2.248
18	CH <sub>2</sub> Cl·CO <sub>2</sub> H . . . . .	45	1.94	3.179
19	CH <sub>3</sub> ·CH:CH·CO <sub>2</sub> H . . . . .	45	1.11	1.36
20	Ph·CH:CH·CO <sub>2</sub> H . . . . .	45	1.18	1.580
21	Ph·C:C·CO <sub>2</sub> H . . . . .	43	2.11 ± 0.04	3.77

Fig. 2 shows some approximate correlations between the dimerisation and acid-dissociation equilibria: (i) The points for seven of the ten substituted benzoic acids are grouped fairly closely about the upper straight line: that for *p*-toluic acid is the only accurately known point to deviate by more than 0.2 in  $\log_{10} K_2$ . The greater the dissociation as an acid in water, the greater the dissociation of the dimer in benzene. (ii) The points representing crotonic, cinnamic, and phenylpropionic acid, which form the third

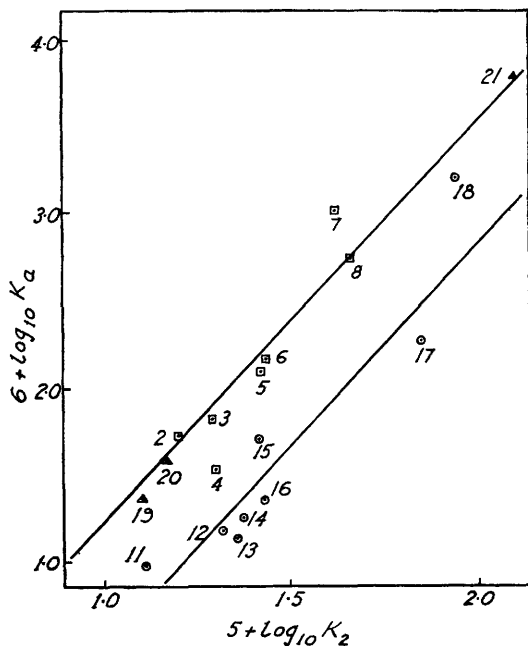


FIG. 2

Comparison of equilibrium constants for dimerisation ( $K_2$ ) and acid dissociation ( $K_a$ ) of carboxylic acids.

$\log_{10} K_a$  at 25° in water (in mole  $l^{-1}$ );  $\log_{10} K_2$  at 30° in benzene (in mole-fraction units).

- Substituted benzoic acids.
- △ Other acids in which conjugation is possible: crotonic, cinnamic, and phenylpropionic acid.
- Acids without conjugation between carboxyl group and rest of molecule.

group in Table 6, lie near the same straight line. Thus there appears to be a general relation covering acids in which the carboxyl group is conjugated with the rest of the molecule. (iii) The points for the second group in Table 6—those in which there is no conjugation between the carboxyl group and the rest of the molecule, including fatty acids and phenylacetic and  $\beta$ -phenylpropionic acid—appear to be grouped about the lower line in Fig. 2. ( $\beta$ -Phenylpropionic acid is thus no longer anomalous, on this classification.) For a given acid strength,  $K_a$ , this line corresponds to less dimerisation,  $K_2$  being larger by a factor of about 2. The data used for all

these acids were obtained from dielectric-constant measurements only, however, and it would be desirable to have confirmatory evidence and values of  $\Delta H_2^\circ$  and  $\Delta S_2^\circ$  from other methods. There are not enough data on acid dissociation constants in benzene to test whether they would give more exact relations between  $K_2$  and  $K_a$ . (iv) The slope of each line is about 2; that is,  $K_a$  is proportional to  $K_2^2$ , or the effects of substituents on the free energy of acid dissociation in water are about twice as great as those on the free energy of dissociation of the dimer in benzene.

Generalising the conclusions, it appears that, to some extent at least, dimerisation and acid strength depend on the same structural factors. The effects of variation in structure are smaller for dimerisation than for acid dissociation, and acids appear to be distinguished according to whether or not mesomeric effects can influence the carboxyl group.

Attempts to interpret these regularities further lead however to difficulties. Unfortunately the experimental results on  $\Delta H_2^\circ$  and  $\Delta S_2^\circ$  are not accurate enough, compared with the rather small variations in  $K_2$  (which is much more accurately known), to allow us to decide how far each of these two quantities contributes to the variations in  $\Delta G_2^\circ$  and  $K_2$ ; the variations of  $\Delta H_2^\circ$  and  $T\Delta S_2^\circ$ , relative to the values for, say, benzoic acid, are comparable with the experimental uncertainties, as may be seen from Table 4. The free energy of acid dissociation will depend, in a series of acids,  $R\cdot CO_2H$ , on the energy of dissociation of the acid molecule to give a hydrogen atom ( $R\cdot CO_2H \rightarrow R\cdot CO_2 + H$ ), on the electron-affinity of the remaining radical ( $R\cdot CO_2 + e \rightarrow R\cdot CO_2^-$ ), and on the energy and entropy of solvation of the anion  $R\cdot CO_2^-$ . It would be difficult to predict *a priori* how these quantities are related to  $\Delta H_2^\circ$  and  $\Delta S_2^\circ$ . (For that matter, we do not know enough about them to predict values of  $K_a$ .) If solvation changes could be ignored, we should conclude *a posteriori* from the experimentally observed relations that the energies of dissociation of dimer to monomer and of monomer to  $R\cdot CO_2^- + H^+$  were linearly related, and that for a given change of substituent the changes in the latter were about double those in the former. However, these simple conclusions are not admissible, because solvation plays an important part in the dimerisation equilibrium, as we have seen, and changes in  $\Delta S_2^\circ$  cannot be neglected; while in determining acid strengths the entropy change is dominant in the lower fatty acids and important also in the substituted benzoic acids, as may be seen from Table 7.<sup>47</sup> More accurate results on a wider range of acids in solution, and extension to aromatic acids of measurements in the vapour phase, must be awaited. The difference in degree of dimerisation observed between the group of acids whose strengths are thought to be controlled by inductive effects only, and those for which mesomeric effects also are important, is another puzzle, because both *I* and *M* effects should affect both the dissociation of hydrogen bonds (through the local dipole moments) and the dissociation of  $R\cdot CO_2H$  as an acid; and there is no reason to expect a great difference in the solvation of the anions, in which mesomeric effects will

<sup>47</sup> Everett and Wynne-Jones, *Trans. Faraday Soc.*, 1939, **35**, 1380; R. P. Bell, "Acids and Bases", Methuen, 1952, p. 57.

not be prominent. If confirmed, the different relations for the two types of carboxylic acid might throw light on the several factors influencing the strengths of these acids.

It might be thought that on the electrostatic view of hydrogen bonds there should be a correlation between the dimerisation constant,  $K_2$ , and the dipole moment,  $\mu$ , of the monomer (which is known for many of the acids) since to a first approximation  $\log K_2$  will vary with  $\mu^2$ . This kind of explanation is only valid, however, when the entropy change in the reaction is constant; <sup>48</sup> moreover, one would need to know the local dipole moments of the hydroxyl and the carboxyl group, not merely the resultant dipole moment of the whole molecule. No correlation is in fact found between the latter and the dimerisation constant.

TABLE 7. *Thermodynamic data for acid dissociation in water at 25°.*

For the first group of acids below, the values given for  $\Delta G_a^\circ$ ,  $\Delta H_a$ , and  $\Delta S_a^\circ$  are relative to benzoic acid; for the second, relative to formic acid. These quantities are given in kcal. mole<sup>-1</sup>. They are independent of concentration units, since they refer to the reaction  $R \cdot CO_2H + R' \cdot CO_2^- \rightleftharpoons R \cdot CO_2^- + R' \cdot CO_2H$ .

Acid	pK	$\Delta G_a^\circ$	$\Delta H_a$	$T\Delta S_a^\circ$
<i>p</i> -MeO-C <sub>6</sub> H <sub>4</sub> -CO <sub>2</sub> H . . .	4.47	+ 0.43	+ 0.76	+ 0.33
CHPh:CH-CO <sub>2</sub> H . . .	4.41	+ 0.33	+ 0.56	+ 0.23
<i>p</i> -C <sub>6</sub> H <sub>4</sub> Me-CO <sub>2</sub> H . . .	4.36	+ 0.24	+ 0.26	+ 0.02
<i>m</i> -C <sub>6</sub> H <sub>4</sub> Me-CO <sub>2</sub> H . . .	4.27	+ 0.11	+ 0.03	- 0.08
BzOH . . .	4.18	0	0	0
<i>o</i> -C <sub>6</sub> H <sub>4</sub> Me-CO <sub>2</sub> H . . .	3.91	- 0.40	- 1.44	- 1.04
<i>m</i> -C <sub>6</sub> H <sub>4</sub> I-CO <sub>2</sub> H . . .	3.85	- 0.42	+ 0.15	+ 0.57
<i>o</i> -C <sub>6</sub> H <sub>4</sub> Cl-CO <sub>2</sub> H . . .	2.92	- 1.75	- 2.51	- 0.76
Et-CO <sub>2</sub> H . . .	4.87	+ 1.53	- 0.13	- 1.66
Pr-CO <sub>2</sub> H . . .	4.82	+ 1.46	- 0.66	- 2.12
Me-CO <sub>2</sub> H . . .	4.75	+ 1.37	- 0.06	- 1.43
H-CO <sub>2</sub> H . . .	3.75	0	0	0
CH <sub>2</sub> Cl-CO <sub>2</sub> H . . .	2.82	- 1.21	- 1.11	+ 0.10

*Association in other solvents.* In solvents which are capable of forming hydrogen-bonded complexes, carboxylic acids associate with the solvent molecules rather than with their own species. Thus they give normal molecular weights in ethers, esters, and ketones <sup>49</sup>; and in freezing dioxan, trichloroacetic acid appears, from cryoscopic measurements, to be entirely monomeric, although it is entirely dimerised in benzene at about the same temperature. A range of solvents was used by Brocklesby, <sup>39</sup> who found from ebullioscopic measurements that oleic acid exists entirely as monomer in boiling ether, dioxan, acetone, or acetic acid. Equilibrium constants for the association of these compounds with carboxylic acids in such solvents as benzene have not yet been measured, but it seems likely that we have here a way of studying quantitatively the association of carboxylic acids with ketones and other donor substances.

<sup>48</sup> Hammett, "Physical Organic Chemistry", McGraw-Hill, 1940, Chap. 3.

<sup>49</sup> Bell, Lidwell, and Vaughan-Jackson, *J.*, 1936, 1798.