Very Strong Hydrogen Bonds formed between Carboxylic Acids and Anions: Trifluoroacetic and Acetic Acids with Acetates and Fluoride

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Studies on very strong H bonds have been extended to the strongest carboxylic acid CF_3CO_2H and its anion. The H bonds $CF_3CO_2^- \cdots H{-}OAc$ (Ac = MeCO), $^-F \cdots H{-}O_2CCF_3$, and $CF_3CO_2^- \cdots H{-}O_2CCF_3$ have been studied in detail by both p.m.r. and i.r. spectroscopy and $\delta(OH)_H$, K_c, $\Delta\nu(O{-}H)$, ΔH^0, ΔG^0, and ΔS^0 values obtained.

GLACIAL acetic acid is a good solvent for certain metal fluorides.[1] In a previous paper [2] the very strong H bonds, $^-F \cdots H{-}OAc$ (Ac = MeCO), formed in these solutions were investigated by p.m.r. spectroscopic methods and values for $\delta(OH)_H$, the chemical shift of the H-bonding proton, obtained. Acetates in acetic acid were also studied. Other thermochemical data, and especially ΔH^0 [obtained from $\Delta\nu(O{-}H)$, the shift of the vibrational mode] and ΔS^0 (obtained from K_c, the dissociation constant in $CDCl_3$ solution) were calculated.

We have recently turned our attention to the acid CF_3CO_2H and its anion. This acid should be a good non-aqueous solvent from the point of view of its low m.p., b.p., and high relative permittivity, ε_r. However it is also a strong acid and this naturally limits the anions which can be studied in it. Since the inception of the present work a report on the use of CF_3CO_2H as a solvent for p.m.r. spectroscopy has been published by Dyer and Jones.[3] This deals with solutions of alkali-metal and some quaternary ammonium trifluoroacetates and in part overlaps with our own studies. These authors find that $\delta(OH)_H$ for the H bond $CF_3CO_2^- \cdots HO_2CCF_2$ varies according to the accompanying cation, moving downfield with increasing cation size. For the ions K^+, Rb^+, and Cs^+ the variation is small, and we found that for the fluorides KF, RbF, and CsF in AcOH $\delta(OH)_H$ values for $^-F \cdots HOAc$ were equal.[2]

As well as studying solutions in carboxylic acids, we have also used a method derived from that used by Martin and Fujiwara [4] to measure $\delta(FHF^-)$ of the difluoride anion. This method employs tetra-n-butylammonium salt solvates which are soluble in $CDCl_3$. By extending the method it is possible to obtain values for K_c and hence ΔG^0 which in turn leads to ΔS^0, a good measure of the strength of a H bond.

EXPERIMENTAL

P.m.r. measurements were made on a Perkin-Elmer R12B spectrometer operating at 60 MHz at 25 °C and referenced internally to Me_4Si. I.r. spectra of the metal-salt solvates were obtained by evaporation of a salt solution on a NaCl disc under reduced pressure until the spectrum showed no absorption due to the free-acid solvent; spectra were recorded on a Perkin-Elmer 457 spectrometer.

Aristar grade glacial AcOH (Ac = MeCO) and trifluoroacetic acid (Ralph Emanuel) were dried over molecular sieves before use. Metal fluorides were commercial samples dried at 100 °C *in vacuo*. The salt $Bu^n{}_4NF$ was prepared as previously described.[2]

Preparations.—Tetra-n-butylammonium acetate. The previous method of preparing this salt from aqueous solution [2] was abandoned in favour of a method [5] based on equation (1), using hot methanol as solvent. Mixed acetate–iodide salt did not form as we had observed with $Bu^n{}_4NI{-}K[OAc]$.[2] The product, an oil, was obtained in 95% yield after filtering off the precipitated AgI. The product was decolourized by boiling in ethyl acetate–diethyl ether with charcoal, and finally recrystallized from $CHCl_3$ as fine white needles, m.p. 118 °C.

$$Bu^n{}_4NI + Ag[OAc] = Bu^n{}_4N[OAc] + AgI(\downarrow) \quad (1)$$

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[1] J. Emsley, *J. Chem. Soc.* (*A*), 1971, 2511.

[2] J. H. Clark and J. Emsley, *J.C.S. Dalton*, 1973, 2154.

[3] R. G. Jones and J. R. Dyer, *J. Amer. Chem. Soc.*, 1973, **95**, 2465.

[4] J. S. Martin and F. Y. Fujiwara, *Canad. J. Chem.*, 1971, **49**, 3071.

[5] J. Steyman and P. M. Lorenz, *J. Amer. Chem. Soc.*, 1966, **88**, 2093.

Tetra-n-butylammonium trifluoroacetate. Equimolar amounts of $Bu^n{}_4NOH$ (40% aq.) and CF_3CO_2H reacted and water was removed under reduced pressure at 70 °C. On cooling, white crystals formed which were washed with diethyl ether and dried *in vacuo*, m.p. 45 °C (Found: C, 60·8; H, 10·1; N, 3·98. $Bu^n{}_4N[CF_3CO_2]$ requires C, 60·9; H, 10·2; N, 3·95%). The tetra-n-butylammonium salt solvates were prepared by dissolving the salts in CF_3CO_2H, generally an exothermic process, removing excess of acid by evaporation at 100 °C, and cooling slowly whereupon white crystals of the solvate were obtained; the crystals are fairly hygroscopic. The composition of the products was confirmed by titration with 0·1M-NaOH. Salt solvates prepared were $Bu^n{}_4NF,CF_3CO_2H$ (m.p. 45), $Bu^n{}_4N[CF_3CO_2],AcOH$ (m.p. 34), and $Bu^n{}_4N[CF_3CO_2],CF_3CO_2H$ (m.p. 54 °C).

Solutions of potassium and rubidium trifluoroacetates. These salts were prepared from the corresponding anhydrous carbonate and trifluoroacetic acid. Solutions in glacial AcOH and CF_3CO_2H were made by warming and shaking the salt with excess of acid for several hours. Dissolution is much less exothermic than that of fluorides in acetic acid. The monosolvates, $CF_3CO_2M,AcOH$ and CF_3CO_2M,CF_3CO_2H, were obtained by evaporation of excess of acid and these are quite stable even on exposure to the atmosphere. Saturated solutions are *ca.* 3·0- and 2·0M-$K[CF_3CO_2]$ in AcOH and CF_3CO_2H respectively and 3·5- and 2·2M-$Rb[CF_3CO_2]$ in AcOH and CF_3CO_2H respectively, determined by evaporation and/or titration methods.

Solutions of potassium fluoride in trifluoroacetic acid. The heat of dissolution of anhydrous KF in CF_3CO_2H is sufficient to make the acid boil, comparable to its behaviour in AcOH. Similarly, the resultant solution needs centrifuging to reduce cloudiness. A saturated solution is 2·75M in KF and is very viscous, again analogous to KF–AcOH.

RESULTS AND DISCUSSION

In a previous paper [2] we made use of two methods of calculating $\delta(OH)_H$. The first, equation (2), is suitable

$$\delta(OH)_{obs} = \delta(OH)_{sol} + (y/x)[\delta(OH)_H + \delta(OH)_{sol}] \quad (2)$$

for dealing with solutions in the acids as solvents, where $\delta(OH)_{obs}$, $\delta(OH)_{sol}$, and $\delta(OH)_H$ are chemical shifts of the hydroxyl proton of the observed solution, pure solvent, and anion H-bonding species; x and y are the number of moles of solvent and solute respectively. The second, equation (3), refers to studies of

$$\delta(OH)_{obs} = \delta(OH)_H + K_c{}^{\frac{1}{2}}m^{-\frac{1}{2}}[\delta(OH)_m - \delta(OH)_H] \quad (3)$$

$Bu^n{}_4NX,HO_2CR$ in $CDCl_3$ solution. In these solutions equilibrium (4) is established, and $\delta(OH)_{obs}$ for this system is a time-averaged value from both that of the H-bonding acid, $\delta(OH)_H$, and the free acid, $\delta(OH)_m$. The latter is assumed to be entirely in the monomeric form under these dilute conditions (see later). In equation (3) $K_c = [RCO_2H][X^-]/[X^- \cdots HO_2CR]$ is used rather than K based on activities, and m is the total concentration in mol kg^{-1} of the salt solvate.

$$X^- \cdots HO_2CR \xrightleftharpoons{K} X^- + RCO_2H \quad (4)$$

Equations (2) and (3) permit $\delta(OH)_H$ to be measured in two independent ways. Equation (3) also allows K_c to be determined, from which ΔG^0 is obtained. To proceed further requires ΔH^0 to be known and for this it has been necessary to turn to i.r. hydroxyl shifts, $\Delta\nu(OH)$. It has been shown that for $^-F \cdots H{-}OAc$ that $\Delta\nu(OH)$ can be used to give a value of ΔH^0 which is in agreement with that obtained from thermochemical measurements.[6] On the strength of this, other ΔH^0 values have been calculated from the corresponding $\Delta\nu(OH)$ values.

Trifluoroacetate in Glacial AcOH.—The above methods have already been applied to solution of fluorides and acetates in acetic acid. Both solutes when added to AcOH increase $\delta(OH)_{obs}$ quite markedly. The addition of any solute to AcOH disturbs the equilibria between the solvent polymers in favour of the dimer, $(AcOH)_2$, which has a higher $\delta(OH)$ value than the other solvent species and hence on dilution $\delta(OH)_{obs}$ increases. The increase is approximately linear and is given by $\delta(OH)_{sol} = 11{\cdot}60 + 0{\cdot}031m$, in other words with a gradient of +0·031 p.p.m. kg mol^{-1} This can be used to 'correct' gradients of plots obtained from solutes such as F^- and AcO^- which form very strong H bonds. In these cases the gradients are much larger than +0·031 p.p.m. kg mol^{-1}.

When $K[CF_3CO_2]$ was added to AcOH to give concentrations of 0—3M the value of $\delta(OH)_{obs}$ was almost stationary over the whole range of concentration at 11·59 ± 0·02 p.p.m., with only a slight increase at higher concentrations: the gradient of the plot of $\delta(OH)_{obs}$ against m was *ca.* +0·007 p.p.m. kg mol^{-1} which means a net gradient of —0·024 p.p.m. kg mol^{-1} when corrected for solvent dilution. In other words the $\delta(OH)_H$ value of the H bond which is being formed between $CF_3CO_2{}^-$ and AcOH is less than that for the bond formed between solvent molecules themselves. From equation (2) the value of $\delta(OH)_H$ was thus calculated to be 11·1 ± 0·5 p.p.m. The second method, using $Bu^n{}_4N[CF_3CO_2],HOAc$ in $CDCl_3$, gave a straight line plot of $\delta(OH)_{obs}$ against $m^{-\frac{1}{2}}$ (Figure) of intercept 11·07 ± 0·05 p.p.m., agreeing nicely with that obtained above. The gradient of this line was $K_c{}^{\frac{1}{2}}[\delta(OH_m - 11{\cdot}07]$ and, using $\delta(OH)_m = 5{\cdot}65$ p.p.m., this gave a value of $K_c = (1{\cdot}14 \pm 0{\cdot}38) \times 10^{-2}$ mol kg^{-1}. Consequently ΔG^0 ($= -RT \ln K_c$) = 11·3 ± 0·9 kJ mol^{-1}.

For the fluoride–acetic acid H bond, ΔH^0 was estimated from thermochemical data to be 120 ± 10 kJ mol^{-1}, and the hydroxyl shift in the i.r. spectrum, $\Delta\nu(OH)$, was 2 200 ± 100 cm^{-1}. The latter figure, when compared with that for $(AcOH)_2$, for which ΔH^0 is 30 ± 2 kJ mol^{-1} and $\Delta\nu(OH)$ 560 ± 50 cm^{-1}, also gave a value for $\Delta H^0(^-F \cdots H{-}OAc)$ of 120 ± 10 kJ mol^{-1}. A conversion factor of $[\Delta\nu(OH)/\Delta H^0] = 18$ cm^{-1} kJ^{-1} mol, justified on this agreement, led to meaningful results with the $AcO^- \cdots H{-}OAc$ system,[2] and is used in this paper. Whilst it is recognized that i.r. shifts (accurate to only ±100 cm^{-1}) give only an approximate value of ΔH^0, and that for some systems agreement

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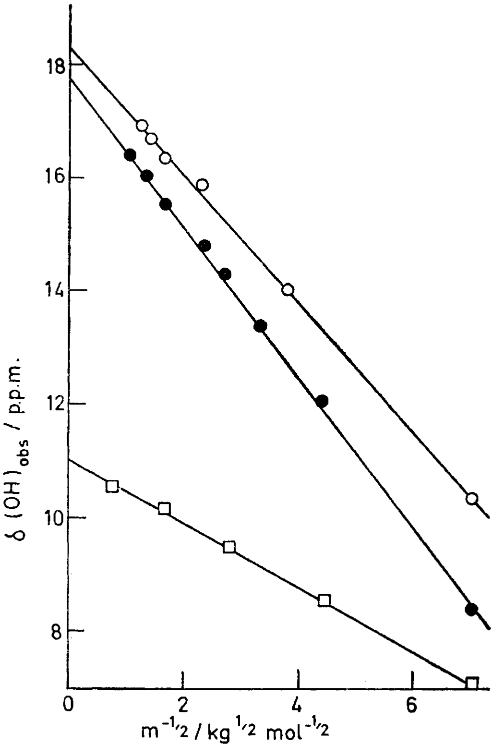
[6] J. Emsley, *J. Chem. Soc.* (*A*), 1971, 2702.

between $\Delta\nu$ and ΔH^0 is virtually non-existent, in our case we feel that similarity in the type of H bond we are studying allows us to use this method with some degree of confidence.

I.r. spectra of the salts $K[CF_3CO_2]$ and $Rb[CF_3CO_2]$ in AcOH were studied. Evaporation of these solutions on NaCl discs gave a dry film of salt solvate whose spectrum could be run after successive pumping operations to remove more and more solvent. The ν(O–H) band was typically very broad, centred at 2 940 ± 100 cm^{-1}, with a weak shoulder at 3 400 cm^{-1}; the monomer peak is at 3 580 cm^{-1}. Exhaustive pumping of the disc eventually removed all the AcOH and this in itself is evidence of a weaker H bond than that formed between F^- or AcO^- and AcOH. $\Delta\nu(OH) = 640 \pm 100$ cm^{-1}, which gives $\Delta H^0 = 36 \pm 6$ kJ mol^{-1}. This leads to a value for ΔS^0 of $+83 \pm 20$ J K^{-1} mol^{-1}, which indicates a less tightly organized H-bonding complex than either $^-F \cdots H{-}OAc$ and $AcO^- \cdots H{-}OAc$, but nevertheless one that is more organized than most H bonds. The Table compares these three H bonds.



Hydroxyl p.m.r. shift, $\delta(OH)_{obs}$, against $m^{-\frac{1}{2}}$ for solutions of $Bu^n_4N[CF_3CO_2],HO_2CCF_3$ (○), $Bu^n_4N[CF_3CO_2],HOAc$ (□), and Bu^n_4F,HO_2CCF_3 (●)

The interesting point the $CF_3CO_2^- \cdots H{-}OAc$ system brings out is that, although this is a stronger bond than that in the acetic acid dimer as measured by ΔH^0 or ΔS^0, it has a lower value for $\delta(OH)_H$, 11·3 ± 0·9 compared to 12·4 p.p.m. There appear to be several factors influencing the chemical shifts of strong H bonds. For example, small cations were shown by Dyer and Jones to shift $\delta(OH)_H$ upfield.[3]

Trifluoroacetates in Trifluoroacetic Acid.—Trifluoroacetic acid as a non-aqueous solvent has the advantages over glacial AcOH of lower m.p. (−15·3 *cf.* +16·6 °C) and b.p. (72·4 *cf.* 118·5 °C), and much higher relative permittivity (40 at 21 °C *cf.* 6·2). The latter physical property actually *increases* with increasing temperature for CF_3CO_2H from 26 at −11 °C to 43 at 28 °C.[7] A study of ε_r of CF_3CO_2H in cyclohexane solution has been used to calculate the association constant for the acid dimer as $K = 320$ l mol^{-1} compared to $K = 21\,000$ l mol^{-1} for the acetic acid dimer.[8]

Trifluoroacetic acid is a very strong acid and this limits its use as a solvent to anions of equally strong or stronger acids. Addition of acetates generates considerable heat and evaporation of excess of solvent from these solutions yields trifluoroacetates. Fluorides on addition of CF_3CO_2H seem to produce solutions comparable to those obtained in AcOH; heat is evolved, the solutions are very viscous, and evaporation yields solvates of the type MF,CF_3CO_2H. Trifluoroacetic acid is therefore a suitable solvent for studying solutions of fluorides and trifluoroacetates, both of which should form very strong H bonds to the solvent.

Like that of AcOH, the $\delta(OH)_{sol}$ value of pure CF_3CO_2H varies over a range of values (11·6 ± 0·1 p.p.m.) and seems to be very sensitive to minute amounts of water and tiny changes of temperature. The best value of $\delta(OH)_{sol}$ for use in equation (2) is that obtained by back extrapolation. Reeves[9] first reported the increase in $\delta(OH)_{sol}$ of CF_3CO_2H on addition of a neutral solute (CCl_4); this increase is much less than that which occurs on dilution of AcOH. A plot of $\delta(OH)_{sol}$ against molality of CCl_4 in CF_3CO_2H showed an increase from 11·62 (pure solvent) to 11·74 p.p.m. (8·77M-CCl_4, 0·50 mol fraction) reaching a maximum of 11·80 p.p.m. (*ca.* 18M-CCl_4, 0·70 mol fraction), thereafter decreasing rapidly to a final extrapolated value of 5·10 p.p.m. at infinite dilution. This latter value in effect represents the $\delta(OH)_m$ value necessary for equation (3). A similar value was obtained with $CDCl_3$ as the solvent. For the range 0—18M-CCl_4 in CF_3CO_2H the value of $\delta(OH)_{sol}$ is given by equation (5) and the gradient of +0·011 p.p.m. kg mol^{-1} from this has been used to ' correct ' values of $\delta(OH)_{obs}$ in this solvent.

$$\delta(OH)_{sol} = 11{\cdot}62 + 0{\cdot}011\text{M} \qquad (5)$$

The system trifluoroacetate in trifluoroacetic acid has been studied by Jones and Dyer[3] mainly by measuring $\delta(OH)_{obs}$ for solutions in CF_3CO_2H. Our method based on equations (2) and (5) for $K[CF_3CO_2]$ gave a straight line (except at very low concentrations) from which $\delta(OH)_H$ was calculated as 17·3 ± 0·5 p.p.m. This is substantially lower than their value for this system. The previous value varied according to the cation [$\delta(OH)_H$ = 15·73 (Li^+), 16·94 (Na^+), 19·17 (K^+), 19·44

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[7] J. H. Simons and K. E. Lorentzen, *J. Amer. Chem. Soc.*, 1950, **72**, 1426.

[8] F. Thyrion and D. Decroocq, *Compt. rend.*, 1965, **260**, 2797.

[9] L. W. Reeves, *Canad. J. Chem.*, 1961, **39**, 1711.

(Rb^+), and 19·80 p.p.m. (Cs^+)]. Using substituted ammonia salts Jones and Dyer obtained $\delta(OH)_H = 19{\cdot}66$ (Me_4N^+) and 19·59 p.p.m. (Me_3NPh^+), although a direct method using the latter salt showed a levelling out of $\delta(OH)_H$ at 18·83 p.p.m. for concentrations of 1 : 1 and higher, *i.e.* $CF_3CO_2^-$–HO_2CCF_3 and with excess of trifluoroacetate. This value they chose as the 'best,' but were aware of the difficulties in studying these systems. The influence of the cation is blamed for some of the variance. In previous work [2] on MF in AcOH we found the fluorides KF, RbF, and CsF gave the same value for $\delta(OH)_H$, which was different to that of Bu^n_4NF in AcOH solutions.

Studies of the monosolvate systems $Bu^n_4N[CF_3CO_2]$,HO_2CCF_3 in $CDCl_3$ offered a better way of obtaining $\delta(OH)_H$ as well as other information. A plot of $\delta(OH)_{obs}$ against $m^{-\frac{1}{2}}$ is shown in the Figure and is linear, confirming the validity of equation (3); from it $\delta(OH)_H = 18{\cdot}23 \pm 0{\cdot}05$ p.p.m., as expected. Also $K_c = (7{\cdot}20 \pm 1{\cdot}28) \times 10^{-3}$ mol kg^{-1} and hence $\Delta G^0 = 12{\cdot}3 \pm 0{\cdot}4$ kJ mol^{-1}.

Physical parameters of very strong hydrogen bonds

	$^-F \cdots HOAc$ [a,b]	$AcO^- \cdots HOAc$ [b]	$^-F \cdots HO_2CCF_3$	$CF_3CO_2^- \cdots HO_2CCF_3$	$CF_3CO_2^- \cdots HOAc$
ΔH^0/kJ mol^{-1}	120 ± 6	105 ± 6	113 ± 6	108 ± 6	36 ± 6
ΔG^0/kJ mol^{-1}	$13{\cdot}0 \pm 0{\cdot}4$	$11{\cdot}1 \pm 0{\cdot}9$	$12{\cdot}2 \pm 0{\cdot}4$	$12{\cdot}3 \pm 0{\cdot}4$	$11{\cdot}3 \pm 0{\cdot}9$
ΔS^0/J K^{-1} mol^{-1}	357 ± 20	313 ± 20	337 ± 20	320 ± 20	83 ± 20
K_c/mol kg^{-1}	$(5{\cdot}4 \pm 1{\cdot}0) \times 10^{-3}$	$(1{\cdot}2 \pm 0{\cdot}4) \times 10^{-2}$	$(7{\cdot}8 \pm 1{\cdot}4) \times 10^{-2}$	$(7{\cdot}2 \pm 1{\cdot}3) \times 10^{-3}$	$(1{\cdot}1 \pm 0{\cdot}4) \times 10^{-2}$
$\delta(OH)_H$/p.p.m. [c]	$14{\cdot}5 \pm 0{\cdot}1$	$15{\cdot}7 \pm 0{\cdot}1$	$17{\cdot}9 \pm 0{\cdot}1$	$18{\cdot}2 \pm 0{\cdot}1$	$11{\cdot}1 \pm 0{\cdot}1$
$\delta(OH)_H$/p.p.m. [d]	$17{\cdot}4 \pm 0{\cdot}5$	$16{\cdot}9 \pm 0{\cdot}5$	$18{\cdot}9 \pm 0{\cdot}5$	$17{\cdot}3 \pm 0{\cdot}5$	$11{\cdot}1 \pm 0{\cdot}5$

[a] See ref. 2. [b] See ref. 1. [c] Bu^n_4X,HO_2CR–$CDCl_3$ Method. [d] KX–HO_2CR Method.

The system $Na[CF_3CO_2]$,$2CF_3CO_2H$ was originally studied 20 years ago using i.r. spectroscopy by Klemperer and Pimental [10] who assigned a broad band at 2 450 cm^{-1} to ν(OH) (Δν = 1 150 cm^{-1}). Closer inspection of their spectra and comparison with ours leads us to believe that the band at 1 650 cm^{-1} is that due to ν(OH). This is much stronger and broader than the weak peak at *ca.* 2 500 cm^{-1}. Furthermore this latter peak eventually disappears from the spectrum of $K[CF_3CO_2]$ and $Rb[CF_3CO_2]$ solutions in CF_3CO_2H when these are evaporated and the solid film pumped dry. These spectra show the two carbonyl-stretching frequencies of $CF_3CO_2^-$ at $1\,670 \pm 100$ cm^{-1} and CF_3CO_2H at $1\,770 \pm 100$ cm^{-1} as broad peaks superimposed on the ν(OH) very broad peak which is centred at $1\,650 \pm 100$ cm^{-1}. No peaks were present in spectra above 1 800 cm^{-1}. The monomer ν(OH) of CF_3CO_2H is at 3 590 cm^{-1}, thus $\Delta\nu = 1\,940 \pm 100$ cm^{-1} and $\Delta H^0 = 108 \pm 6$ kJ mol^{-1} and $\Delta S^0 = 320 \pm 20$ J K^{-1} mol^{-1}, comparable to values for other very strong H bonds (Table).

Fluorides in Trifluoroacetic Acid.—Acetates are almost completely protonated when dissolved in trifluoroacetic acid, which is much stronger than acetic acid. The anion species present in these solutions is consequently $CF_3CO_2^- \cdots HO_2CCF_3$, as i.r. studies showed. In water HF is a stronger acid than AcOH, but weaker than CF_3CO_2H, and so it might be expected that fluorides in CF_3CO_2H would also be protonated. However water is an exceptional solvent for HF and in other solvents such as AcOH it behaves as a strong acid. Its Hammett acidity function (−10·98) shows it to be of comparable strength to H_2SO_4 (−11).[11,12] Its strength in CF_3CO_2H is not known but our results suggest that it is a very strong acid and that equilibrium (6) lies well to the left.

$$CF_3CO_2H + F^- \rightleftharpoons CF_3CO_2^- + HF \qquad (6)$$

P.m.r. studies of KF in CF_3CO_2H gave $\delta(OH)_H = 18{\cdot}9 \pm 0{\cdot}5$ p.p.m., whereas Bu^n_4F,CF_3CO_2H in $CDCl_3$ gave a value of $17{\cdot}85 \pm 0{\cdot}05$ p.p.m. As the Figure shows, a straight line was again obtained from which $K_c = (7{\cdot}8 \pm 1{\cdot}4) \times 10^{-3}$ mol kg^{-1} was calculated and consequently $\Delta G^0 = 12{\cdot}2 \pm 0{\cdot}4$ kJ mol^{-1}.

The i.r. spectrum of a film of KF,CF_3CO_2H obtained by evaporation provides the best evidence that a very strong H bond has been formed. It also proves that reaction (6) has not occurred since the spectrum is unlike those of such species as $K[CF_3CO_2]$ and $K[CF_3CO_2]$,HO_2CCF_3. The spectrum is dominated by a broad flat-top peak very similar to that of KF,AcOH and centred at $1\,550 \pm 100$ cm^{-1} corresponding to a shift, Δν(OH), of $2\,040 \pm 100$ cm^{-1}. This produced values of ΔH^0 of 113 ± 6 kJ mol^{-1} and ΔS^0 of 337 ± 20 J K^{-1} mol^{-1}.

Values of $\delta(OH)_H$ and thermochemical data are collected in the Table for the systems discussed above and the two systems reported previously. Enthalpy, entropy, and free-energy factors show that the order of H-bond strengths in these systems is: $^-F \cdots HOAc > {}^-F \cdots HO_2CCF_3 \geqslant CF_3CO_2^- \cdots HO_2CCF_3 > AcO^- \cdots HOAc > CF_3CO_2^- \cdots HOAc$. P.m.r. studies do not give values for $\delta(OH)_H$ by either the Bu^n_4NX,HO_2CR–$CDCl_3$ or KX–HO_2CR method which can be related to this order. The effects of ion-pairing are probably more important in the latter method and so it is preferable to use the order of $\delta(OH)_H$ produced by the former which is: $CF_3CO_2^- \cdots HO_2CCF_3 > {}^-F \cdots HO_2CCF_3 > AcO^- \cdots HOAc > {}^-F \cdots HOAc > CF_3CO_2^- \cdots HOAc$.

Three factors should affect shielding at the H-bonding proton: (i) a shift contribution arising from the magnetically anisotropic carboxylate group which should be absent from the spherically symmetrical ion F^-; (ii) the symmetry of the H bond (in very strong symmetrical

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[10] W. Klemperer and G. C. Pimental, *J. Chem. Phys.*, 1954, **22**, 1399.

[11] H. H. Hyman, T. I. Lane, and T. A. O'Donnell, Abstr. 145th Meeting Amer. Chem. Soc., 1963, 63T.

[12] H. H. Hyman and J. J. Katz, 'Non-aqueous Solvent Systems,' ed. T. C. Waddington, Academic Press, London, 1965, pp. 47—81.

H bonds, which have a potential-energy minimum at the midpoint, the proton is in the least-shielded position); and (iii) an electron-withdrawing group, such as CF_3, attached to the carbonyl group. Also arising from this last point one would expect CF_3CO_2H to be a better H-bond donor than AcOH, but $CF_3CO_2^-$ to be a poorer H-bond acceptor than AcO^-. This explains why the system $CF_3CO_2^- \cdots HOAc$ has the weakest H bond. Also weaker H bonds of this type will have two potential minima and the H atom will be situated near the parent acid and thus be more shielded.

Taking into consideration these three factors we can see how the order of $\delta(OH)_H$ values arises; the H bond in $CF_3CO_2^- \cdots HO_2CCF_3$ should give a larger value than $^-F \cdots HO_2CCF_3$ and $AcO^- \cdots HOAc$ than $^-F \cdots HOAc$ according to points (i) and (ii). Moreover the value for $CF_3CO_2^- \cdots HO_2CCF_3$ will be larger than that for $AcO^- \cdots HOAc$, and $^-F \cdots HO_2CCF_3$ than that for $^-F \cdots HOAc$ according to point (iii). Thus the whole order can be explained. These explanations should also account for the value of $\delta(FHF^-)$ for the difluoride ion studied by Martin and Fujiwara in a similar system.[4] They found $\delta(FHF^-) = 16{\cdot}3$ p.p.m., which places it between the values for $^-F \cdots HO_2CCF_3$ and $AcO^- \cdots HOAc$. We might have expected the value for $\delta(FHF^-)$ to exceed even that of $CF_3CO_2^- \cdots HO_2CCF_3$, according to points (ii) and (iii), but the effect of two spherical fluorine species makes point (i) doubly important for this system.

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