Ab initio Studies of the Strongest Type of Hydrogen Bond: Carboxylic Acid–Fluoride Systems

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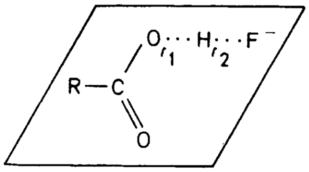
Ab initio LCAO–MO–SCF calculations have been performed on the acetic acid–fluoride system and the strength of the hydrogen bond, $MeCO_2H \cdots F^-$, is found to be as strong as that previously reported for the formic acid–fluoride system. The implications of this and its relationship to other physical parameters of these hydrogen bonds are discussed. The carboxylic acid–fluoride systems are capable of forming esters with simple alkyl halides. The enhanced nucleophilicity of RCO_2H has been shown to be due to the increased negative charge of the hydroxy oxygen atom induced by the formation of the very strong hydrogen bond to the fluoride ion.

WE recently reported[1] the results of *ab initio* LCAO–MO–SCF calculations on the simplest of the carboxylic acid–fluoride systems, $HCO_2H \cdots F^-$. These showed that the hydrogen bond had an energy of *ca.* 250 kJ mol^{-1}, putting it firmly in the class of very strong hydrogen bonds, and ahead even of the bifluoride ion. We have now extended our calculations to the more complex system, $MeCO_2H \cdots F^-$, to see whether this comparable system exhibits the same strength of hydrogen bonding. It does.

In other papers we have pursued two aspects of these carboxylic acid–fluoride systems: first we have studied their physical properties and in particular their i.r. spectra and the chemical shift of the hydrogen bonding proton in the ^1H n.m.r. spectra;[2,3] and secondly we have investigated their ability to act as strong carboxylating reagents as in their behaviour towards simple alkyl dihalides when diesters are formed.[4] Both these aspects can now be reinterpreted in the light of our calculations of the energy of this type of hydrogen bond and of the net charges on the hydroxy oxygen atom in these molecules and hydrogen bond complexes.

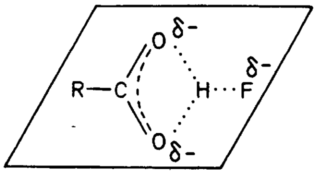
Details of the Calculations.—Recent theoretical studies on the systems $F{-}H \cdots F^-$ [5] and $HO{-}H \cdots F^-$ [6,7] have demonstrated that the contribution of the molecular extra correlation energy to the hydrogen bond energy amounts to only *ca.* 5%. Thus Hartree–Fock calculations of the strength of hydrogen bonds formed between closed-shell molecules should yield reliable results, provided that the basis set employed in the calculations is sufficiently complete.

In this study *ab initio* LCAO–MO–SCF calculations have been performed on $MeCO_2^-$, $MeCO_2H$, and $MeCO_2H \cdots F^-$ using a version of the program GAUSSIAN 70[8] which has been modified to incorporate the technique of level-shifting the Hartree–Fock Hamiltonian[9] directly in the AO basis.[10] Initially the experimental geometry of acetic acid[11] was taken and, using a minimal STO-3G basis set,[12] the value of r(OH) in $MeCO_2H$ was optimized to 99 pm, and the values of r(OH) and r(HF) in $MeCO_2H \cdots F^-$ were optimized to 140 and 99 pm, respectively. In both cases the conformation of the methyl group with the carbonyl group eclipsed was found to be the most stable and the H–F bond axis was assumed to be collinear with the O–H bond axis in the molecular plane, (I).



(I)

R = H : r_1 138 ; r_2 99 pm
R = Me : r_1 140; r_2 99 pm



(II)

Calculations for the hydrogen bond energy were then performed using the [4*s*,2*p*/2*s*,1*p*] extended Gaussian basis sets of atomic orbitals reported by Dunning[13] with an *s* orbital scaling factor of $\sqrt{2}$ and a *p* orbital exponent of 0.7 for the acidic proton, while the scaling factors and *p* exponents of the methyl protons were all set at unity. It has recently been demonstrated that this basis yields hydrogen bond energies for $HCO_2H \cdots F^-$ and $F{-}H \cdots F^-$ which are stable against further extensions of

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[11] ' Interatomic Distances,' ed. L. E. Sutton, Special Publication No. 11, The Chemical Society, 1958, p. M82S: r(CH) 108.0; r(CC) 149.7; r(C=O) 124.5; r(C–O) 131.2; r(H $\cdots$ H) 173.3 pm; $\widehat{HCH}$ 106.8; $\widehat{CC}{=}O$ 119.5; $\widehat{OCO}$ 130.0 (from p. M132); and $\widehat{COH}$ 107.8°.

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the basis set.[1] The use of level-shifters was found to be essential to ensure the convergence of the SCF calculations on $HCO_2H \cdots F^-$ and $MeCO_2H \cdots F^-$ with extended basis sets.

The results of the present calculations on $MeCO_2H \cdots F^-$ are displayed in the Table together with the corresponding details of our previous results for $HCO_2H \cdots F^-$ and $F{-}H \cdots F^-$ in order to facilitate direct comparison. It is clear that the strength of the hydrogen bond in $MeCO_2H \cdots F^-$ is comparable with that in $HCO_2H \cdots F^-$, both of which are stronger than the hydrogen bond in the bifluoride anion.

Total energies (hartrees) and hydrogen bond energies (kJ mol^{-1}) calculated for the systems $MeCO_2H \cdots F^-$, $HCO_2H \cdots F^-$, and $F{-}H \cdots F^-$

X	$MeCO_2$	HCO_2	HCO_2	F [a]	F [a]
Basis set	[4*s*,2*p*/2*s*,1*p*]	[4*s*,2*p*/2*s*,1*p*]	[5*s*,3*p*/3*s*,1*p*]	[4*s*,2*p*/2*s*,1*p*]	[5*s*,3*p*/3*s*,1*p*]
$E(X^-)$	−227.180 331	−188.145 664	−188.159 340	−99.414 059	−99.417 548
$E(XH)$	−227.752 001	−188.715 599	−188.731 579	−100.038 590	−100.042 946
$E(XH \cdots F^-)$	−327.260 822	−288.224 912	−288.242 375	−199.536 412	−199.542 035
$\Delta E(XH \cdots F^-)$	249	250	245	220	214 [b]

[a] For HF, $r(HF) = 91.7$ pm, and for HF_2^-, $r(HF) = 113.8$ pm. [b] Erroneously quoted as 217 kJ mol^{-1} in ref. 1.

Similar calculations have also been performed on the acetate and formate anions with $r(CO)$ 127.9 pm, and $\widehat{OCO}$ 124.4°, in order to attempt to distinguish the nucleophilic species responsible for esterification of alkyl halides in acetic acid–fluoride solutions. The results indicate that $MeCO_2H \cdots F^-$ is more stable (by 110 kJ mol^{-1}) than acetate plus hydrogen fluoride, and it seems likely that the hydrogen bonded species is in fact the esterifying agent.

DISCUSSION

The effect that the fluoride ion has on the carboxy-group can only be interpreted by the assumption that a hydrogen bond of the type $RCO_2H \cdots F^-$ has been formed. Moreover, this hydrogen bond is not the normal kind of weak interaction but is a very strong hydrogen bond. Its formation has a profound influence on the chemistry of the acid. Nowhere is the power of this hydrogen bond demonstrated more dramatically than in the effect it has on the course of organic reactions.[4] Similar very strong hydrogen bonds between organic molecules and fluoride ions are also producing unexpected results.[14–16]

Hydrogen Bond Calculations.—Although these are the first *ab initio* calculations to be reported for $HCO_2H \cdots F^-$ and $MeCO_2H \cdots F^-$ to our knowledge, there are several *ab initio* calculations of the hydrogen bond energy in $F{-}H \cdots F^-$ with which to compare our results. In particular values similar to ours have been obtained by Kollman and Allen [17] (217), Almlöf [18] (213), Roos *et al.*[5] (222 and 234), and Neckel *et al.*[19] (234 kJ mol^{-1}). In addition, a somewhat smaller value has been reported by Noble and Kortzeborn [20] (167 kJ mol^{-1}) using a basis set which yields a much more accurate description of fluorine than hydrogen. These authors also estimate a value of 117 kJ mol^{-1} from the results of McLean and Yoshimine [21] where a more nearly complete basis set was used for HF than for HF_2^-. In view of these considerations the last two values quoted should be treated with some caution.

On the experimental side, the bifluoride hydrogen bond energy has been estimated *via* lattice energies, which are unfortunately somewhat uncertain due to various assumptions which have to be made.[22] Values of 155,[23] 176,[24] 243,[25] and 252 [26] kJ mol^{-1} have been obtained. Our calculated value of 220 kJ mol^{-1} thus falls well within the span of experimental results and is in good agreement with the consensus of theoretical values.

Until now, the strongest known asymmetric hydrogen bond was that in $HO{-}H \cdots F^-$ with an experimentally determined energy of 97 kJ mol^{-1}.[27] This system has been thoroughly investigated in *ab initio* calculations by Clementi *et al.*[7,28,29] and by Diercksen *et al.*[6,30,31] The most recent calculations,[6,7] taking into account electron correlation and zero-point vibrations, give hydrogen bond energies in excellent agreement with experiment. The $O{-}H \cdots F^-$ bond is calculated to be very nearly linear with $r(O{-}H)$ 100 and $r(H \cdots F)$ 150 pm. This situation is in striking contrast with our results for the $RCO_2H \cdots F^-$ systems where the $O \cdots H$ bond is found to be much longer than the $H \cdots F$ bond in (I).

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[31] W. Kraemer and G. Diercksen, *Theor. Chim. Acta*, 1972, **27**, 265.

In fact, the value of $r(\mathrm{H \cdots F})$, 99 pm, in carboxylic acid–fluoride systems is not much greater than that in the free HF molecule (91.7 pm).

Previous attempts to measure the energy of the hydrogen bond formed between $\mathrm{MeCO_2H}$ and $\mathrm{F^-}$ led to a value of *ca.* 120 kJ mol^{-1}.[32] This figure was arrived at from thermochemical data and was supported by i.r. measurements. Both sets of data need to be re-examined in the light of our present work, which suggests hydrogen bond energies of double this value.

In the calculation of the hydrogen bond energy from the thermochemical results it was necessary to estimate the lattice energy of $\mathrm{K^+,MeCO_2HF^-}$, and a value of 734 kJ mol^{-1} was chosen, based on Kapustinski's method of calculating lattice energies from 'thermochemical radii'. This in turn required a value for the radius of the hydrogen bonded anion which was assumed to be the same as the acetate ion, since this was the only comparable anion for which a value (159 pm) was available.

Reversing this sequence of events, and starting with the new hydrogen bond energy of 250 kJ mol^{-1}, now permits us to calculate the lattice energy of $\mathrm{KF,MeCO_2H}$ as 606 kJ mol^{-1}, and the 'thermochemical radius' of the hydrogen bonded anion as 226 pm. This last figure is less than the sum of the radii of the acetate and fluoride ions which is 292 pm.

I.r. Spectrum of $\mathrm{RCO_2H \cdots F^-}$.—The shift of the stretching vibration, $\Delta\nu$, of a bond that participates in hydrogen bond formation has been used to derive values for hydrogen bond strengths. Comparing $\Delta\nu$(OH) of acetic acid dimer (560 cm^{-1}) with that of acetic acid–fluoride (2 200 cm^{-1}) suggested that the hydrogen bond in the latter was four times stronger than the former, were a linear relationship to hold. Clearly it does not, since the hydrogen bond strength of the dimer is 30 kJ mol^{-1}, which is only one-eighth of the strength of the acetic acid–fluoride hydrogen bond.

Our model of the carboxylic acid–fluoride hydrogen bond shows the proton to reside nearer to the F than its parent O. It is thus a moot point whether $\Delta\nu$ should be $\Delta\nu$(OH) or $\Delta\nu$(HF). The former yields shifts of $2\,150 \pm 100$ cm^{-1}[33] while the latter is $2\,350 \pm 100$ cm^{-1}.* It is $\Delta\nu$(HF) which is to be compared to $\Delta\nu$(HF) of $\mathrm{HF_2^-}$ which is also in the range $2\,450 \pm 100$ cm^{-1}. If $\Delta\nu$(HF) is directly proportional to hydrogen bond energy then the i.r. evidence supports $\mathrm{HF_2^-}$ having a stronger bond. The lack of accuracy in determining $\Delta\nu$(HF), or $\Delta\nu$ of any very strong hydrogen bond for that matter, makes this method of calculating bond energies from i.r. shifts very unreliable.

In a previous publication[3] we discussed a puzzling aspect of the i.r. spectra of $\mathrm{RCO_2H}$–CsF solutions which was the presence of a broad band centred at *ca.* 2 140 cm^{-1}. These we wrongly ascribed to vibrations of a bifurcated hydrogen bond of type (II) which we reported[1] as too unstable relative to (I). However it is relatively stable, being only 35 kJ mol^{-1} less stable than (I) and may make a meaningful contribution to the i.r. spectrum. Alternatively these bands may be assigned to the first overtone, $2\nu_b$, of the hydrogen bond bending mode which occurs at *ca.* 1 170 cm^{-1}.[32]

^{1}H *N.m.r. Shifts.*—On addition of fluoride to carboxylic acids the signal arising from the hydroxy proton shifts to higher values.[2,3] The solutions will dissolve a great deal of fluoride but they become so viscous that their ^{1}H n.m.r. spectra cannot be recorded. Consequently it has been necessary to extrapolate to obtain δ(OH) for the 1 : 1 system corresponding to $\mathrm{RCO_2H \cdots F^-}$. In the case of CsF solutions different values were obtained depending upon the acid: $\delta(\mathrm{OH, HCO_2H \cdots F^-})$ 19.7; $\delta(\mathrm{OH, MeCO_2H \cdots F^-})$ 15.0; $\delta(\mathrm{OH, EtCO_2H \cdots F^-})$ 13.8; and $\delta(\mathrm{OH, PrCO_2H \cdots F^-})$ 13.8. These results were thought to reflect pK_a values; the more easily the H is released by the O, the more it is attracted to $\mathrm{F^-}$ and the less shielded it finds itself. This rationalization is wrong. Our calculations show the $\mathrm{O \cdots F^-}$ hydrogen bond to be the same in both formic acid and acetic acid–fluorides with the proton located as in (I).

In some symmetrical very strong hydrogen bonds the proton has been located at the mid-point of the bond; *e.g.* in $[\mathrm{F \cdots H \cdots F}]^-$ it is 113 pm from each F. For this species also the δ value of the proton has been reported at 16.3[34] consistent with its being at the region of minimum electron density. In our model H approaches $\mathrm{F^-}$ more closely and we would therefore expect a more shielded proton and a lower value of δ as the values for $\mathrm{MeCO_2H \cdots F^-}$, $\mathrm{EtCO_2H \cdots F^-}$, and $\mathrm{PrCO_2H \cdots F^-}$ show. Based as they are on very long extrapolations they are within experimental error of one another. But this is not the case with $\mathrm{HCO_2H \cdots F^-}$. Formic acid presents special problems insofar as its suitability as a solvent for ^{1}H n.m.r. is concerned[3] and no reliance can be placed on the extrapolation method.

For the system $\mathrm{MeCO_2H \cdots F^-}$ the value of δ(OH) has been obtained by an alternative method, which gave 14.5.[2] Taking this in conjunction with the other values, it would seem to suggest that δ(OH) of the hydrogen bonding proton in the carboxylic acid–fluoride systems is to be found in the 14—15 region of the spectrum. This is in accord with the asymmetry of this bond which increases the shielding of the proton by the fluoride atom compared to the bifluoride situation, and that in other symmetric hydrogen bonds such as $[\mathrm{MeCO_2 \cdots H \cdots O_2CMe}]^-$ where δ(OHO) is 15.7[2] and $[\mathrm{CF_3CO_2 \cdots H \cdots O_2CCF_3}]^-$ where it is 18.8.[35]

Esterification.—Heating carboxylic acids and simple alkyl halides under reflux does not produce esters. The use of metal and quaternary ammonium carboxylates is

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* All the i.r. spectra of $\mathrm{RCO_2H}$–CsF (R = H, Me, Et, or Pr) contain the characteristic broad band centred at $1\,550 \pm 100$ cm^{-1} that is assigned to ν_s(OHF).[3]

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necessary to effect carboxylation, probably because the use of these salts permits higher reaction temperatures.[36] Similarly the employment of KF in reactions of carboxylic acids and alkyl halides will give good yields of esters, free from by-products.[4]

The presence of F^- must result in the formation of a very strong hydrogen bond which by implication must produce a more nucleophilic centre at the oxygen end of the hydrogen bond. Apart from the calculated stability of $MeCO_2H \cdots F^-$ with respect to $MeCO_2^- + HF$, further support for this assertion can be deduced from an examination of the Mulliken charges on the nucleophilic hydroxy oxygen atom in the three species: the acetate anion, acetic acid itself, and the acetic acid–fluoride combination. These charges are calculated to be —0.6 (acetate), —0.4 (acetic acid), and —0.7 (acetic acid–fluoride), demonstrating the activation of the hydroxy oxygen as a nucleophile by the formation of the hydrogen bond to fluoride.

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