A Proton Nuclear Magnetic Resonance Study of Hydrogen Bonding between Fluoride and the Enol Form of Pentane-2,4-dione and Other β-Diketones

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The dependence of the hydroxy proton chemical shift of the enol form of pentane-2,4-dione upon the concentration of added fluoride has been determined in acetonitrile solution. Two methods involving tetra-n-butylammonium fluoride solvates and potassium fluoride–18-crown-6 complexes are described for carrying the fluoride anion into solution. Solutions containing mole ratios of pentane-2,4-dione : $\bar{F}$ of up to 50 : 1 show ^{1}H n.m.r. spectra consistent with the diketone existing entirely in the enol form. The estimated value for the chemical shift of the 1 : 1 complex $\delta(OH\bar{F})$, is *ca.* 13 p.p.m. upfield from that of the pure enol. Similar results are obtained for the enol forms of 1,3-diphenylpropane-1,3-dione and 2-acetylcyclopentanone. ^{1}H N.m.r. studies of competitive hydrogen bonding between acetic acid and pentane-2,4-dione for fluoride anions suggests that the former is the better hydrogen-bond electron acceptor.

THE n.m.r. method has been widely used for the study of *strong* anionic hydrogen bonding.[1–6] The change in the chemical shift of the hydrogen-bonding proton for example, on increasing the concentration of the electron donor (the anion), is toward lower field relative to the unassociated electron acceptor, as would be expected. The magnitude of such changes is perhaps less predictable, often being *ca.* 10 p.p.m. or more.[1–4,7,8]

The fluoride anion is one of the most powerful hydrogen-bond electron donors and its ability to form strong hydrogen bonds to a variety of protic organics has been illustrated on several occasions.[1–3,9] Recently, it has been shown that fluoride forms a strong hydrogen bond to the enol form of β-diketones [10] to such an extent that the resulting solvates are very useful sources of the carbanion and behave as a valuable precursor in the synthesis of *C*-alkylated β-diketones,[11] *C*-sulphenylated β-diketones,[12] and substituted hydroxyacetophenones.[13]

The present study was undertaken partly to elucidate the effects of the fluoride anion on the keto–enol tautomerism of β-diketones and on hydrogen bonding in the enol form of pentane-2,4-dione in particular. To the best of our knowledge this represents the first deliberate attempt to investigate the interaction of fluoride with an intramolecularly hydrogen-bonded substance. Two methods for carrying the fluoride anion into solution have been investigated. The successful application of crown ether complexes of potassium fluoride to such studies may prove to be of wide significance in the field of anionic hydrogen bonding in general. The use of tetra-alkylammonium fluoride solvates for studies involving the fluoride anion is also demonstrated.

EXPERIMENTAL

Materials.—Reagent grade pentane-2,4-dione and acetonitrile were purified by ordinary methods and were stored over 5 Å molecular sieves. AristaR grade acetic acid was dried over 5 Å molecular sieves before use. 1,3-Diphenylpropane-1,3-dione was recrystallised from ether. 2-Acetylcyclopentanone and other solvents were dried by ordinary methods. 18-Crown-6 was a commercial sample used as obtained. Potassium fluoride was dried by heating at 100 °C *in vacuo* for several hours.

The tetrabutylammonium fluoride and its solvates were prepared by methods described elsewhere.[11] All solvates were recrystallised from anhydrous *NN*-dimethylformamide as white or pale yellow crystals. Once pure, the solvates could be stored in a dry atmosphere without appreciable decomposition occurring, although the 2-acetylcyclopentanone solvate underwent a slow colour change from white to brown. The solvates were used within 24 h of purification. M.p.s (recorded on a Mettler FP5 digital temperature read-out using a Mettler FP52 hot stage) of the solvates are: Bu$_4{}^n$NF,pentane-2,4-dione, 136—138 °C; Bu$_4{}^n$NF,1,3-diphenylpropane-1,3-dione, 124—125 °C; and Bu$_4{}^n$NF,2-acetylcyclopentanone, 101—102 °C.

Sample Preparation.—Solutions for n.m.r. spectral determinations were prepared in glass vials with polyethylene caps by dilution of solutions of the 1 : 1 complexes with the β-diketone. The K(crown)$^+$F(β-diketone)$^-$ complexes were prepared in solution (acetonitrile) and no attempt was made to isolate these solvates. The closed vials were weighed before and after the introduction of each sample component.

^{1}H *N.m.r. Spectra.*—Measurements were made using a Perkin-Elmer R-10 spectrometer operating at 60 MHz at 25 °C. N.m.r. tubes of 5.00 mm outside diameter were rinsed with the solution under investigation then filled with *ca.* 1 ml of solution containing a few mg of tetramethylsilane as internal standard. All spectra were recorded at amplitude and radiofrequency field adjustments that provided the maximum signal to noise ratio. Solutions containing relatively high concentrations of fluoride gave spectra with very broad OH resonances and it was usually not possible to measure $\delta(OH)_{obs}$ to better than ±0.1 p.p.m. for solutions of $\bar{F}$: β-diketone mole ratio greater than *ca.* 1 : 10. Under the conditions used, there was no evidence for definite splitting due to coupling with ^{19}F although the ^{19}F n.m.r. spectrum of a concentrated solution of Bu$_4$NF-

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[11] J. H. Clark and J. M. Miller, *J.C.S. Perkin I*, 1977, 1743.

[12] J. H. Clark and J. M. Miller, *Canad. J. Chem.*, 1978, **56**, 141.

[13] J. H. Clark and J. M. Miller, *J.C.S. Perkin I*, 1977, 2063.

(pentane-2,4-dione) in chloroform does show splitting of the fluorine resonance at −50 °C.[11] Detailed low temperature ^{19}F and ^{1}H n.m.r. studies on these complexes will be reported in a later article. There was also a somewhat smaller broadening and relatively small but steady upfield shift in the CH resonance for solutions of pentane-2,4-dione and 1,3-diphenylpropane-1,3-dione. The hydroxy peaks in solutions of fluoride in acetic acid–pentane-2,4-dione mixtures were relatively sharp and could usually be measured to ±0.03 p.p.m. The percentage of keto and enol tautomer reported here were found by taking the averaged integrated intensity of the appropriate peaks over several spectra for each solution and are accurate to better than ±5%.

Choice of Solvent.—Although acetonitrile is potentially bifunctional in hydrogen-bonding terms, this capacity is probably low enough to render its effects on an $\bar{F}$ . . . enol complex negligible. It is interesting to note that chloroform, in which Bu_4NF solvates are generally soluble, proves to be a poor choice for our systems. Other solvents in which such solvates are soluble such as water, alcohols, and carboxylic acids may be discounted on the basis of their own hydrogen-bonding abilities, whereas benzene, which has often been used as a solvent for crown ether complexes, has previously been shown to be capable of extensive association with β-diketones.[14]

METHODS AND RESULTS

The first difficulty that is often encountered on undertaking a study of anionic hydrogen-bonding in solution is a practical one, that of solubilization of the salt. The advent of polar aprotic solvents went some way to overcome this problem but the use of such solvents is only of limited applicability. Alkali-metal fluorides are only soluble in *NN*-dimethylformamide for example to the extent of *ca.* 3% even at close to reflux temperatures.[9] Perhaps the most significant advances in this field have been as a result of the use of tetra-alkylammonium salts which are often soluble in a number of organic solvents. The greatest drawback in the use of such materials is in the hygroscopic nature of those salts of relatively small anions such as fluoride and chloride. In particular, tetra-alkylammonium fluorides are extremely difficult to handle because of their affinity for water. The recent increase in interest in these fluorides as bases in synthetic chemistry[10–13,15–19] has resulted in a disproportionate amount of time being devoted to rendering these compounds anhydrous. The advantages to the synthetic chemist of using anhydrous material are as apparent as those to the hydrogen-bonding chemist, especially when one considers that the fluoride anion undoubtedly operates in a hydrogen-bonding role in many of its reactions.[10–13] One possible solution to this problem lies in the awareness that water is held to the fluoride anion by hydrogen bonding and that by providing an alternate hydrogen-bonding site for the fluoride, a non-aqueous solution of the fluoride may be prepared.[11,13]

The advent of crown ethers has provided a widely applicable method for the introduction of metal salts into aprotic organic solvents. Although the enhanced solubility of potassium fluoride in aprotic solvents containing crown ethers has been utilised on a number of occasions in synthetic work,[20–22] the significance of this solubilisation or indeed of that of any salt, to anion solvation studies has been neglected.

Potassium (18-*Crown*-6) *Fluoride–Pentane*-2,4-*dione Solutions in Acetonitrile.*—Plots of molality M of KF (18-crown-6 complex) in pentane-2,4-dione (enol form) against the observed hydroxy n.m.r. shift $\delta(OH)_{obs}$ for complex concentrations of 0.4 and 0.1 molal in acetonitrile are linear and provide relationships (1) and (2), respectively.

$$\delta(OH)_{obs} = 15.42 - 1.35M \tag{1}$$

$$\delta(OH)_{obs} = 15.44 - 1.32M \tag{2}$$

The complex is soluble to *ca.* 0.4 molal in MeCN which is chosen as a suitable ' inert ' (in a hydrogen-bonding sense) solvent (see later). To a good approximation the results for 0.4 and 0.1 molal (complex in MeCN) fall on the same straight line which suggests that at these concentrations of fluoride, equilibrium (3) lies almost entirely in favour of the anionic hydrogen-bonded complex.

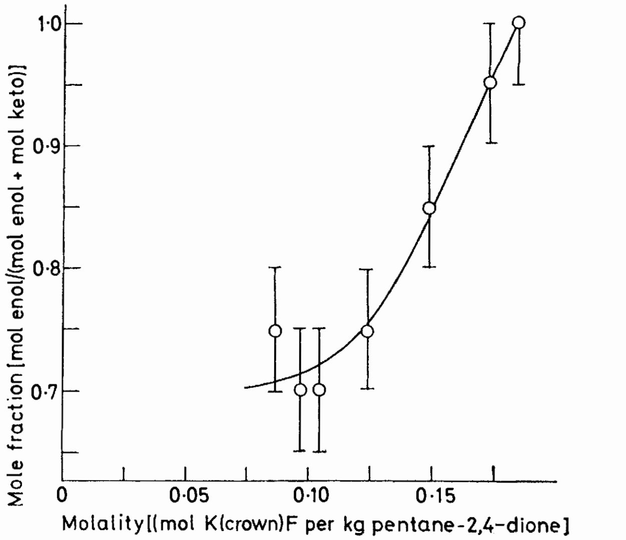

FIGURE 1 Mole fraction of enol present against the molality of solutions of KF(18-crown-6) in pentane-2,4-dione. The concentration of fluoride in acetonitrile (the bulk solvent) is 0.4 molal

$$\bar{F} + \text{enol} \rightleftharpoons F(\text{enol})^- \tag{3}$$

The effect of added complex on the mole fraction of enol present is shown in Figure 1. The β-diketone appears to be entirely in the enol form up to mole ratios of β-diketone : $\bar{F}$ of 50 : 1.

Tetrabutylammonium Fluoride–Pentane-2,4-*dione Solutions in Acetonitrile and Chloroform.*—Plots of molality M of $Bu_4{}^nNF$ (added as the pentane-2,4-dione monosolvate) in pentane-2,4-dione (enol form) against the observed hydroxy n.m.r. shift $\delta(OH)_{obs}$ for complex concentrations of 0.4 and 0.1 molal in MeCN and 0.3 molal in $CHCl_3$ are

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[22] C. L. Liotta and H. P. Harris, *J. Amer. Chem. Soc.*, 1974, **96**, 2250.

linear and provide relationships (4)—(6) respectively. The results for both concentrations in MeCN are again in good agreement.

$$\delta(\mathrm{OH})_{\mathrm{obs}} = 15.53 - 1.29M \qquad (4)$$

$$\delta(\mathrm{OH})_{\mathrm{obs}} = 15.58 - 1.31M \qquad (5)$$

$$\delta(\mathrm{OH})_{\mathrm{obs}} = 15.45 - 0.65M \qquad (6)$$

The different slope for the $CHCl_3$ solutions is undoubtedly due to competition between the enol and $CHCl_3$ for $\bar{F}$. Although $CHCl_3$ is the weaker hydrogen-bond electron acceptor, its ability to solvate small anions is accepted [23] and the effect of added fluoride on the $CHCl_3$ n.m.r. resonance is the expected downfield shift [$\delta(CHCl_3)$ 7.70 ± 0.15 over the concentration range investigated].

Fluoride-1,3-*Diphenylpropane*-1,3-*dione and Fluoride*-2-*Acetylcyclopentanone Solutions in Acetonitrile.*—The above methods were applied to acetonitrile solutions of 1,3-diphenylpropane-1,3-dione and 2-acetylcyclopentanone using the 18-crown-6 complex of KF and tetrabutylammonium fluoride–β-diketone solvate as the sources of the fluoride ion. Molalities of fluoride in MeCN of 0.1 or 0.2 were chosen on the assumption that equilibrium (3) lies almost entirely in favour of the anionic solvate for both β-diketones as it appears to do for pentane-2,4-dione. The results give linear plots of molality M of fluoride in enolised β-diketone against $\delta(\mathrm{OH})_{\mathrm{obs}}$ for 1,3-diphenylpropane-1,3-dione–$Bu_4{}^nNF$ (fluoride is 0.1 molal in MeCN); 1,3-diphenylpropane-1,3-dione–KF(18-crown-6) (complex is 0.2 molal in MeCN); 2-acetylcyclopentanone–$Bu_4{}^nNF$ (fluoride is 0.2 molal in MeCN); 2-acetylcyclopentanone–KF(18-crown-6) (complex is 0.2 molal in MeCN); and 2-acetylcyclopentanone–$Bu_4{}^nNF$ (fluoride is 0.2 molal in $CHCl_3$) and provide relationships (7)—(11), respectively.

$$\delta(\mathrm{OH})_{\mathrm{obs}} = 16.8 - 2.80M \qquad (7)$$

$$\delta(\mathrm{OH})_{\mathrm{obs}} = 16.9 - 3.06M \qquad (8)$$

$$\delta(\mathrm{OH})_{\mathrm{obs}} = 12.8 - 1.20M \qquad (9)$$

$$\delta(\mathrm{OH})_{\mathrm{obs}} = 12.9 - 1.26M \qquad (10)$$

$$\delta(\mathrm{OH})_{\mathrm{obs}} = 12.8 - 0.52M \qquad (11)$$

Fluoride Solutions in Pentane-2,4-*dione–Glacial Acetic Acid Mixtures.*—^1H N.m.r. spectra of solutions containing constant KF : acetic acid mole ratios and also of those containing constant KF : (acid + enol) mole ratios were recorded. One time-averaged hydroxy resonance was observed for each fluoride solution whereas corresponding solutions containing no fluoride give two distinct hydroxy peaks.[14] The extent of enolisation of pentane-2,4-dione was between 70 and 80% for all the solutions investigated.

DISCUSSION

Keto–enol tautomerism in β-diketones is an important subject in organic chemistry and in co-ordination chemistry. Although it is generally accepted that non-polar, inert (in a hydrogen-bonding sense) solvents favour the enol form, the situation with potential hydrogen-bonding solvents is less clear Amines appear to favour the enol form of pentane-2,4-dione for example to the extent that no keto peaks are seen in the n.m.r. spectra of solutions of the diketone in triethylamine up to a mole fraction of the diketone of 0.84.[24] This is presumably due to the formation of strong enol–amine hydrogen bonds.[24] However, other strong hydrogen-bond electron donors such as dimethyl sulphoxide favour the keto form [14] which suggests that the hydrogen-bonding potential of the solvent must be balanced with its polarity, which reduces the electrostatic repulsion between the carbonyl groups of the keto molecules, and the effect of increased solubility of the keto tautomer in such solvents. Here we see that in the presence of the hydrogen-bond electron donor fluoride anion, enolisation of pentane-2,4-dione is complete up to diketone: $\bar{F}$ mole ratios of 50 : 1. This is undoubtedly the most dramatic effect on the keto–enol equilibrium that has been reported. Since such small quantities of fluoride are required for complete enolisation, this may well prove to be of value in organic and organometallic chemistry.*

The effect of added fluoride on the ^1H n.m.r. of the three β-diketones investigated here, is to shift the hydroxy resonance upfield relative to that in the pure enol. The signal observed is a time-averaged resonance of the enol molecule in all environments: without $\bar{F}$ in the bulk solvent, as the cation solvation sphere in the bulk solvent, and with $\bar{F}$, in the bulk solvent. Previous studies into the effects of solvents on the $\delta(\mathrm{OH})_{\mathrm{obs}}$ of pentane-2,4-dione and other β-diketones have shown that for MeCN, the change in $\delta(\mathrm{OH})_{\mathrm{obs}}$ over the concentration range 0—100% diketone, is 0.25 p.p.m., and for $CHCl_3$ as solvent, the corresponding change is *ca.* 0.5 p.p.m.[14] We have carried out similar studies here for MeCN, $CHCl_3$, and MeCN–18-crown-6 solutions of the β-diketones over the concentration ranges of interest and found that the change in $\delta(\mathrm{OH})_{\mathrm{obs}}$ is no more than ±0.3 p.p.m. in any one case. This is small compared to the changes observed on adding fluoride, and may be ignored. The effect on $\delta(\mathrm{OH})_{\mathrm{obs}}$ due to cation solvation is probably of minor importance since the cations used are large. The small differences observed between $Bu_4{}^nN^+$ and $K(crown)^+$ may be due to different degrees of ion-pairing. The third contributing factor, that of strong hydrogen-bonding between enol and $\bar{F}$, has the largest effect on $\delta(\mathrm{OH})_{\mathrm{obs}}$.

If all the $\bar{F}$ is assumed to be solvated by enol molecules, we may write a Gutowsky and Saika [25] type of weighted equation (12) for $\delta(\mathrm{OH})_{\mathrm{obs}}$; x and y are the

$$\delta(\mathrm{OH})_{\mathrm{obs}} = [y\delta(\mathrm{OH}\bar{F}) + (x - y)\delta(\mathrm{OHO})]/x \qquad (12)$$

number of moles of enol and $\bar{F}$ respectively, $\delta(\mathrm{OH}\bar{F})$ is the chemical shift of the 1 : 1 complex, and $\delta(\mathrm{OHO})$ is that of the neutral enol in MeCN. Since the variation of $\delta(\mathrm{OHO})$ over the concentration range investigated is

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* It is possible that fluoride not only alters the keto–enol equilibrium extensively but also increases the keto–enol conversion rate so that at very low fluoride concentrations we may be dealing with a highly mobile equilibrium between different hydrogen-bonded species where exchange takes place *via* the keto tautomer as a short-lived intermediate state. For the purpose of our calculations we have assumed that throughout the concentration ranges studied in the fluoride systems, the β-diketones exist entirely in the enol form.

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[24] L. W. Reeves, *Canad. J. Chem.*, 1975, **35**, 1351.

[25] H. S. Gutowsky and A. Saika, *J. Chem. Phys.*, 1953, **21**, 1688.

small, we may assume it is constant and rearrange (12) to (13). This predicts the linear plots observed of slope

$$\delta(\mathrm{OH})_{\mathrm{obs}} = \delta(\mathrm{OHO}) + y[\delta(\mathrm{OH}\bar{\mathrm{F}}) - \delta(\mathrm{OHO})]/x \quad (13)$$

$[\delta(\mathrm{OH}\bar{\mathrm{F}}) - \delta(\mathrm{OHO})]/x$ and of intercept $\delta(\mathrm{OHO})$. It is perhaps, an oversimplification to assume that the graphs remain linear to a molality corresponding to $1\bar{\mathrm{F}} : 1$ enol; however, previous ^{1}H n.m.r. investigations of strong anionic hydrogen bonding [1-4] including other $(\mathrm{FHO})^-$ type hydrogen bonds [1-3] have provided corresponding linear plots. If we assume linearity we may derive values for $\delta(\mathrm{OH}\bar{\mathrm{F}})$ for the various systems studied here. The collected values for $\delta(\mathrm{OH}\bar{\mathrm{F}})$ are in the Table.

The values for $\delta(\mathrm{OH}\bar{\mathrm{F}})$ in the Table suggest that on hydrogen bonding to F, the enol hydroxy proton of a β-diketone experiences an increase in shielding relative to that in the pure enol. It is generally recognised that when the electron donor in a hydrogen bond is other than an aromatic π-electron system, the chemical shift of the hydrogen-bonding proton moves towards lower field, and that the magnitude of the downfield shift is closely related to the hydrogen-bond strength. One of the most striking manifestations of strong anionic hydrogen bonding has usually been recognised as a large downfield shift in the chemical shift of the hydrogen-bonding proton relative to that in the self-associated electron acceptor.[1-4] This has been attributed to an increase in hydrogen-bond strength.[1-4]

Estimated hydrogen-bond proton chemical shifts for fluoride-enolised β-diketone complexes

	$\delta(\mathrm{OH}\cdots\bar{\mathrm{F}})$	$\Delta\delta(\mathrm{OH})$ [a]
$[\mathrm{K(crown)}]^+ [\mathrm{F(HOC(Me){:}CHCOMe)}]^-$, 0.4 molal in MeCN	1.9 ± 2.5	13.8 ± 2.6
$[\mathrm{K(crown)}]^+ [\mathrm{F(HOC(Me){:}CHCOMe}]^-$, 0.1 molal in MeCN	2.2 ± 2.1	13.5 ± 2.2
$[\mathrm{Bu_4N}]^+ [\mathrm{F(HOC(Me){:}CHCOMe}]^-$, 0.4 molal in MeCN	2.6 ± 2.0	13.1 ± 2.1
$[\mathrm{Bu_4N}]^+ [\mathrm{F(HOC(Me){:}CHCOMe}]^-$, 0.1 molal in MeCN	2.5 ± 2.0	13.2 ± 2.1
$[\mathrm{Bu_4N}]^+ [\mathrm{F(HOC(Me){:}CHCOMe}]^-$, 0.3 molal in $\mathrm{CHCl_3}$	9.0 ± 1.5	6.7 ± 1.6
$[\mathrm{K(crown)}]^+ [\mathrm{F(HOC(Ph){:}CHCOPh)}]^-$, 0.2 molal in MeCN	3.4 ± 1.5	13.6 ± 1.6
$[\mathrm{Bu_4N}]^+ [\mathrm{F(HOC(Ph){:}CHCOPh)}]^-$, 0.1 molal in MeCN	4.4 ± 1.0	12.6 ± 1.1
$[\mathrm{K(crown)}]^+ [\mathrm{F(HOC(Me){:}\overline{C(CH_2)_3C}{:}O)}]^-$, 0.2 molal in MeCN	2.8 ± 1.0	10.2 ± 12.
$[\mathrm{Bu_4N}]^+ [\mathrm{F(HOC(Me){:}\overline{C(CH_2)_3C}{:}O)}]^-$, 0.2 molal in MeCN	3.2 ± 1.0	9.8 ± 1.2
$[\mathrm{Bu_4N}]^+ [\mathrm{(HOC(Me){:}\overline{C(CH_2)_3C}{:}O)}]^-$, 0.2 molal in $\mathrm{CHCl_3}$	8.6 ± 1.5	4.4 ± 1.7

[a] The difference between δ(OH) of the pure enol and $\delta(\mathrm{OH}\cdots\bar{\mathrm{F}})$.

That the $\bar{\mathrm{F}}$ . . . enol hydrogen bond is stronger than that in the pure enol seems certain when one considers the strength of comparable hydrogen bonds,[1,2,26] the remarkable stability of the $\mathrm{Bu_4NF}$ complexes,[11] and the dramatic change in the δ(OH) value of the enol.

Rogers and Burdett [14] suggested, on the basis of extensive ^{1}H n.m.r. studies on β-diketone solutions, that the hydroxy proton is at higher field when involved in an intermolecular hydrogen bond than in an intramolecular hydrogen bond. However, the reported infinite dilution chemical shifts $\delta(\mathrm{OH})_0$ for solutions of pentane-2,4-dione in solvents of vastly different hydrogen-bonding capacities were all within 1.1 p.p.m. of that of the pure enol.[14] Reeves,[24] however, estimated a $\delta(\mathrm{OH})_0$ for pentane-2,4-dione in triethylamine of at least 8 p.p.m. to the high field side of that of the pure enol. It seems likely that the inconsistency in these literature values is due to an inability to detect the δ(OH) peak at low concentrations of enol due to considerable line-broadening and, in some cases, the steady fall in the enol : keto mole ratio at low diketone concentrations.[14]

The dilution curve for the pentane-2,4-dione–triethylamine system reported by Reeves [24] shows the characteristic sharp change in δ(OH) at low enol concentrations corresponding to severe disruption of enol self-association. The position of this sharp change is a reflection of the relative stabilities of the self-associated enol and the enol–solvent complex. That no significant change occurs in the $\delta(\mathrm{OH})_{\mathrm{obs}}$ of amine–enol systems below a concentration of 50 mole % amine, whereas $\bar{\mathrm{F}}$ causes an immediately significant change in the $\delta(\mathrm{OH})_{\mathrm{obs}}$ of the enol is a clear illustration of the relative strength of the $\bar{\mathrm{F}}\cdots$ enol hydrogen bond.

An important consequence of the low enol concentrations at which the marked change in $\delta(\mathrm{OH})_{\mathrm{obs}}$ will occur on most dilution curves and the difficulty in detecting the $\delta(\mathrm{OH})_{\mathrm{obs}}$ at the low enol concentrations is that any extrapolated $\delta(\mathrm{OH})_0$ values must be very approximate. We suggest that the hydroxy proton chemical shift of a hypothetical non-hydrogen-bonded enolised β-diketone would be to the high field side of its $\bar{\mathrm{F}}$ complex and that the corresponding chemical shifts of amine–enol or most other heteromolecular–enol complexes should lie between these two values. Should the value for $\delta(\mathrm{OH}\bar{\mathrm{F}})$ be *ca.* 2—4, then δ(OH) for the non-hydrogen-bonded enol might well be expected to be on the high field side of the tetramethylsilane signal (most anionic hydrogen bonds show a Δδ relative to the 'free' monomer of 10 ± 5 p.p.m.[1-4,7,8]). Intuitively, this seems unlikely; however, one need look no further than Schneider's pioneering work on the n.m.r. of associated hydroxy compounds to find a $\delta(\mathrm{OH})_{\mathrm{obs}}$ for 'free' ethanol (gaseous sample) of within 1 p.p.m. of the $\mathrm{Me_4Si}$ signal.[27]

That the δ(OH) values of $\bar{\mathrm{F}}\cdots$ enol complexes are to the high field side of those of the pure enols when the anionic complexes apparently contain the stronger hydrogen bond is presumably a result of the unique environment of the proton in the chelated structure of the pure enol. The δ(OH) of enolised β-diketones is a poor indication of the strength of the intramolecular hydrogen bond as can be seen by comparing the δ(OH) of intermolecular associated hydroxy compounds [*e.g.* pure phenol, $\delta(\mathrm{OH})_{\mathrm{obs}}$ 5.6] and by noting the wide range

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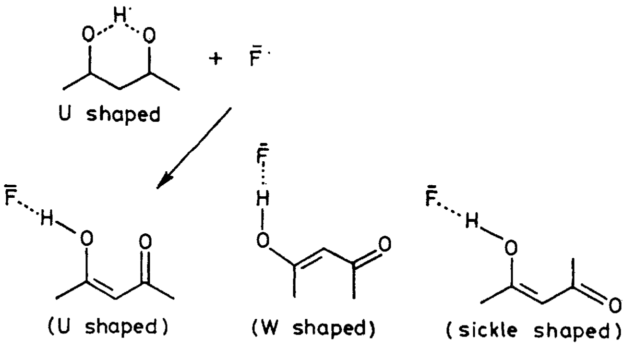
[26] S. A. Harrell and D. H. McDaniel, *J. Amer. Chem. Soc.*, 1964, **86**, 4497.

[27] W. G. Schneider, 'Hydrogen Bonding,' ed. D. Hadzi, London, 1959, p. 55.

of δ(OH) values found for chelated enols (*ca.* 11—*ca.* 18).[28,29]



(14)

On hydrogen bonding to F the chelated structure of enolised β-diketones is presumably destroyed and the resulting complex may adopt one of three conformations [reaction (14)] although for cyclic β-diketones such as 2-acetylcyclopentanone, only the **U** shaped and sickle-shaped conformers are geometrically possible.

However, the estimated chemical shifts for these complexes are at considerably higher field than those of other strongly hydrogen-bonded complexes and this may indicate that the hydrogen-bonding proton is partly shielded by the fluoride ion. Such an effect would become important when there was a significant contribution from the charge-transfer interaction, $\bar{\mathrm{O}} \cdots \mathrm{H{-}F}$. An appreciable amount of HF covalent bond character in very strong hydrogen bonds of this type is by no means unreasonable and has been proposed before for similar complexes.[3]

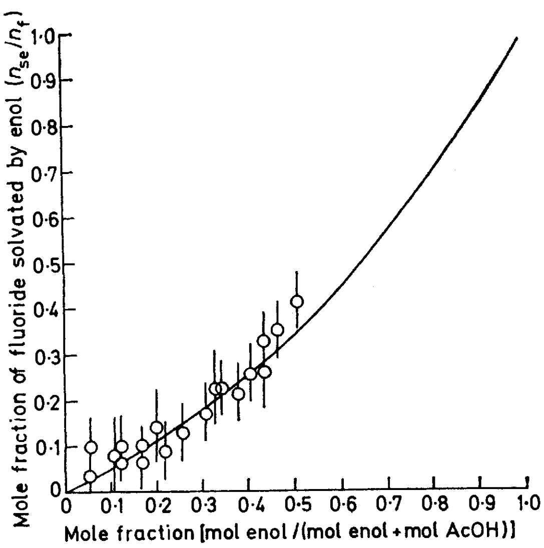


FIGURE 2 Mole fraction of fluoride solvated by enol n_{se}/n_f against mole fraction of enol present in solutions of KF–pentane-2,4-dione–acetic acid

*Competitive Hydrogen Bonding between Acetic Acid and Pentane-*2,4-*dione.*—We have so far described two possible methods for the investigation in solution of anionic hydrogen bonding where solubility problems might normally prevent such studies. A third method is to study ternary systems of the type MX–RZH–R′YH where MX is soluble in one of the two hydrogen-bond electron acceptors. Here we investigate the $KF{-}CH_3CO_2H{-}CH_3COCH_2COCH_3$ system where KF is soluble in CH_3CO_2H.[30] Only one time-averaged, hydroxy proton resonance is seen for this system at various mole ratios which means that unless both protic species compete equally for F, the resulting $\delta(OH)_{obs}$–mole fraction enol plot cannot be linear. However, the observed values do provide an opportunity to investigate the relative abilities of the two protic species to solvate F.

If we start with n_f, n_a, and n_e* moles of KF, acetic acid, and enolised pentane-2,4-dione, respectively, the condition (15) exists at equilibrium, assuming all the F is solvated; n_{se} is the number of moles of enol solvated by fluoride.

$$\begin{array}{ccccccccc} \mathrm{F} & + & \mathrm{AcOH} & + & \mathrm{enol} & \rightleftharpoons & \mathrm{F(AcOH)} & + & \mathrm{F(enol)} \\ 0 & & (n_a - n_f + n_{se}) & & (n_e - n_{se}) & & (n_f - n_{se}) & & n_{se} \end{array} \qquad (15)$$

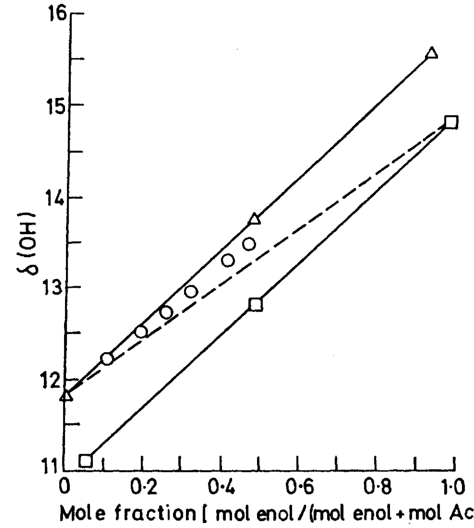


FIGURE 3 ¹H N.m.r. shift of hydroxy proton δ(OH) against mole fraction of enol present in solutions of KF–pentane-2,4-dione-AcOH where the mole ratio KF:(enol + acid) is 1 : 20: 0, observed values; △, calculated values for all fluoride bonded to acid $\{\delta(OH) = [n_f\delta(OH)_{sa} + (n_a - n_f)\ \delta(OH)_a + n_e\delta(OH)_e]/(n_a + n_e)\}$; □, calculated values for all fluoride bonded to enol $\{\delta(OH) = [n_f\delta(OH)_{se} + (n_e - n_f)\delta(OH)_e + n_e\delta(OH)_a]/(n_a + n_e)\}$

The observed hydroxy proton resonance is a weighted average of the acid and enol in all environments: (1) self-associated acid; (2) self-associated enol; (3) enol–acid and keto–acid complexes; (4) as cation solvation spheres; (5) as anion solvation molecules. The effects of (1)—(3) would be seen in a 'blank' run of acetic

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* $n_e = \left|\dfrac{\%\ \text{enol observed}}{100} \times n_{\text{diketone}}\right|$.

[28] L. C. Nonhebel, *Tetrahedron*, 1968, **24**, 1869.

[29] Z. Yoshida, H. Ogoshi, and T. Tokumitsu, *Tetrahedron*, 1970, **26**, 2987.

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

acid–pentane-2,4-dione mixtures. Reeves recorded the n.m.r. spectra of such solutions and observed two distinct hydroxy peaks for the acid and for the enol.[24] The only hydroxy peak to shift appreciably in the concentration range 100% acid–100% enol was that of the enol, by *ca.* 0.25 p.p.m. For the purpose of these calculations we must ignore the effect of (4) on $\delta(\text{OH})_{\text{obs}}$. We can now write a weighted equation (16) for $\delta(\text{OH})_{\text{obs}}$

$$\delta(\text{OH})_{\text{obs}} = [(n_{\text{f}} - n_{\text{se}})\delta(\text{OH})_{\text{sa}} + (n_{\text{a}} - n_{\text{f}} + n_{\text{se}})\delta(\text{OH})_{\text{a}} + n_{\text{se}}\delta(\text{OH})_{\text{se}} + (n_{\text{e}} - n_{\text{se}})\delta(\text{OH})_{\text{e}}]/[n_{\text{a}} + n_{\text{e}}] \quad (16)$$

where $\delta(\text{OH})_{\text{sa}}$ and $\delta(\text{OH})_{\text{se}}$ are the shifts of the KF $\cdots$ HOAc and KF $\cdots$ enol complexes respectively and $\delta(\text{OH})_{\text{a}}$ and $\delta(\text{OH})_{\text{e}}$ are the shifts of the acid and enol respectively, not involved in anion solvation. Rearranging (16) we obtain (17) and taking $\delta(\text{OH})_{\text{sa}}$ 16.7,* $\delta(\text{OH})_{\text{a}}$ 11.6 [being the observed $\delta(\text{OH})$ for the pure acid], $\delta(\text{OH})_{\text{se}}$ 2.3 (the average of the values determined here); taking values for $\delta(\text{OH})_{\text{e}}$ (15.65—15.40) and n_{e} found at each concentration [$\delta(\text{OH})_{\text{e}}$ from 'blank' acid–pentane-2,4-dione runs] we may plot $n_{\text{se}}/n_{\text{f}}$ against $n_{\text{e}}/(n_{\text{e}} + n_{\text{a}})$, *i.e.* the fraction of fluoride ions solvated by enol against the fraction of enol molecules available. Collected values are plotted in Figure 2. The error bars in Figure 2 represent the $n_{\text{se}}/n_{\text{f}}$ values calculated on substituting $n_{\text{e}} = 0$ into equation (17). As can be seen from Figure 2, the results suggest that over the concentration range investigated, fluoride is preferentially solvated by acetic acid molecules. This is perhaps better illustrated by comparing the experimental plot of $\delta(\text{OH})_{\text{obs}}$ against $n_{\text{e}}/(n_{\text{e}} + n_{\text{a}})$ to lines which represent the hypothetical situations of (a) all $\overline{\text{F}}$ bonded to acid and (b) all $\overline{\text{F}}$ bonded to enol. This is shown in Figure 3 for the case where $(n_{\text{a}} + n_{\text{e}}) = 20n_{\text{f}}$ at all concentrations.

$$n_{\text{se}} = [n_{\text{f}}\delta(\text{OH})_{\text{sa}} + (n_{\text{a}} - n_{\text{f}})\delta(\text{OH})_{\text{a}} + n_{\text{e}}\delta(\text{OH})_{\text{e}} - (n_{\text{e}} + n_{\text{a}})\delta(\text{OH})_{\text{obs}}]/[\delta(\text{OH})_{\text{sa}} + \delta(\text{OH})_{\text{e}} - \delta(\text{OH})_{\text{a}} - \delta(\text{OH})_{\text{se}}] \quad (17)$$

All points lie nearest the hypothetical acid line as is expected. A further point worth noting is that the observed chemical shifts clearly show that $\delta(\text{OH})_{\text{se}}$ must be lower than $\delta(\text{OH})_{\text{e}}$ so that the $\delta(\text{OH})_{\text{obs}}$ values never go above the hypothetical acid line.

I am indebted to Mr. D. Goldsworthy for a generous gift of 2-acetylcyclopentanone and to a referee for his suggestions.

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* Determined by extratrapolation of the $\delta(\text{OH})_{\text{obs}}$ values for KF–AcOH solutions.[1]