Fluorine-19 Nuclear Magnetic Resonance Studies of Tetraethylammonium Fluoride in Glacial Ethanoic Acid

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The ^{19}F n.m.r. spectra of solutions of tetraethylammonium fluoride in glacial ethanoic acid are consistent with $F(MeCO_2H)_x^-$ being the only significant fluoride species at concentrations above 0.01 mole fraction (0.004 mol kg^{-1}). Below this the fluoride signal shifts upfield indicating an equilibrium involving a protonated fluoride postulated as $[HF\cdots H^+\cdots O_2CMe^-]$. The chemical shifts [p.p.m. ($CFCl_3$)] of these species in this medium are −123 $[F(MeCO_2H)_x^-]$ and −217 $[HF\cdots H^+\cdots O_2CMe^-]$. There is no evidence for HF_2^- as previously assumed.

Since the discovery that carboxylic acids make excellent solvents for ionic fluorides[1] there has been speculation over the composition of these solutions.[2–9] The original suggestion, that the fluoride ion was solvated *via* very strong hydrogen bonds ($F^-\cdots H\cdots O_2CMe$), has been supported by a variety of evidence.[2–14] However, other evidence has indicated the presence of HF and even HF_2^- in these solutions,[15] a not unreasonable supposition in terms of the acidic nature of the solvent. The ^{19}F n.m.r. spectrum of KF in methanoic acid was interpreted in terms of four equilibria between F^-, HF, HF_2^-, and $(HF)_2$. The i.r. spectrum of KF in $MeCO_2H$ has also been quoted as evidence for HF_2^- being present, especially in aged solutions.[16] It was to clarify the nature of these solutions that we have investigated the system NEt_4F–$MeCO_2H$ by ^{19}F n.m.r. spectroscopy.

Experimental

Tetraethylammonium fluoride was supplied as a hydrate (Aldrich). Complete dehydration in the solid state leads to decomposition.[17] After preliminary drying under reduced pressure the fluoride was dissolved in glacial $MeCO_2H$ and the solution dried by azeotropic distillation with benzene under reduced pressure. The moisture content, measured on a Mitsubishi CA-02 coulometric moisturemeter, was thereby reduced to 150 p.p.m. Dried solutions were made up in a nitrogen purged–P_2O_5 dried glove-box. Fluoride solutions were handled in Polythene containers. Fluorine-19 n.m.r. spectra were run on a Bruker WM 250 spectrometer (235 MHz) operating at a probe temperature of 25 °C. Solutions were manipulated using plastic syringes and C_6F_6 was added to provide a check on the fluoride content of solutions. A sealed concentric Wilmad tube containing CD_2Cl_2 was fitted to provide a deuterium lock. Trichlorofluoromethane was used as an internal reference. Samples were run in both glass and Teflon-lined n.m.r. tubes but as the former showed no etching provided the contents and tube were kept dry, glass tubes were preferred. The results are given in Table 1.

Table 1. ^{19}F N.m.r. observations on solutions of NEt_4F in $MeCO_2H$ at 25 °C

$100x_F$[a]	$[NEt_4F]$/mol kg^{-1}	$\delta_{obs.}$[b]/p.p.m.	$W_{\frac{1}{2}}$[c]/Hz
0.025	0.004	−164.7	490 ± 70
0.05	0.008	−157.4	500 ± 100
0.10	0.017	−148.0	460 ± 130
0.20	0.034	−140.4	660 ± 70
0.30	0.050	−136.7	670 ± 100
0.40	0.067	−135.0	540 ± 10
0.50	0.084	−133.6	540 ± 50
0.52	0.091	−134.3	500 ± 100
1.04	0.182	−130.0	660 ± 50
1.55	0.273	−129.6	426 ± 26
2.06	0.364	−128.4	412 ± 12
2.57	0.455	−128.2	442 ± 14
3.08	0.546	−128.0	410 ± 5
3.58	0.637	−128.0	436 ± 5
4.08	0.728	−127.7	450 ± 5

[a] Mole fraction of NEt_4F, $x_F = [NEt_4F]/([NEt_4F] + [MeCO_2H])$. [b] To the nearest 0.1 p.p.m. upfield of $CFCl_3$. [c] $W_{\frac{1}{2}}$ = Peak width at half peak height.

Deuteriated ethanoic acid, $MeCO_2D$, supplied by Aldrich as 98 atom %, was dried over A4 molecular sieves prior to use until the water content was less than 150 p.p.m. The deuterium content was checked by comparison of the CH_3 and residual OH signals. Solutions of NEt_4F (mole fraction 0.03; concentration 0.50 mol kg^{-1}) in ethanoic acid with various deuterium contents were studied by ^{19}F n.m.r. spectroscopy at 25 °C and the observed chemical shifts at different % D were −127.8 (0), −126.4 (39.8), −126.1 (49.2), −125.5 (71.8), and −124.6 p.p.m. (96.6% D). A broad ^{19}F n.m.r. resonance signal with a half-width of *ca.* 600 Hz was observed in each case.

A solution of NEt_4F in $MeCO_2H$ (mole fraction 0.03) had its ^{19}F n.m.r. spectrum recorded several times over a period of 3 weeks. No change was observed. Our previous report[16] of HF_2^- forming in solutions of KF–$MeCO_2H$ is not supported by ^{19}F n.m.r. evidence, albeit on much more dilute solutions.

Results and Discussion

The behaviour of the signal of the ^{19}F n.m.r. spectrum of NEt_4F–$MeCO_2H$ (Figure) can only be explained in terms of contributions from two very different fluorine environments which exchange rapidly compared to the n.m.r. time-scale. The downfield environment is the fluoride ion, the chemical shift of which varies according to the medium although not in any obvious manner (see Table 2). The nature of the high-field species is more debatable, and within the limits of ^{19}F n.m.r. measurement on the most dilute solutions it would appear to be HF rather than HF_2^-.

The published report which bears most closely on the present work is that of Coulombeau *et al.*,[15] who studied KF, HF, and KHF_2 solutions in pure methanoic acid and in methanoic acid

Table 2. ^{19}F N.m.r. chemical shifts of F^-, HF_2^-, and HF in various solvents

System[a]	$\delta(CFCl_3)^b$/p.p.m.	Reference	System[a]	$\delta(CFCl_3)^b$/p.p.m.	Reference
F^-			HF_2^-		
$NPr^n_4F/CH_2Cl_2/41$	−115[c]	*d*	$NBu^n_4HF_2/MeCN$/*f*	−144	*h*
KF/water/30	−117	18	KHF_2/HCO_2H/*f*	−146	15
$KF/MeCO_2H/30$	−117	18	$NEt_4HF_2/CH_3CN/34$	−149	*i*
$NEt_4F/MeCO_2H/25$	−123	This work	$NEt_4HF_2/HCONMe_2/34$	−149	*c*
KF/water/30	−124	*e*	$NPr^n_4HF_2/CH_2Cl_2/41$	−149	*d*
$KF/HCO_2H–HCO_2K$/*f*	−126	15	$NBu^nH_3HF_2$/liquid/30	−150	*g*
NBu^n_4F/liquid/30	−128	*g*	NEt_3HHF_2/CH_2Cl_2/*f*	−152	*j*
$KF/HCO_2H/30$	−133	18	$NEt_4HF_2/MeNO_2/34$	−154	*i*
$KF/(CH_2OH)_2/30$	−133	18	$NBu^n_2H_2HF_2$/*k*/30	−158	*g*
	(av. −124)		$NBu^n_3HHF_2$/liquid/30	−162	*g*
			$NBu^n_4HF_2$/liquid/30	−168	*g*
				(av. −153)	
HF					
$HF/Me_2SO/34$	−168	*i*	$HF/Et_2O/34$	−188	*d*
$HF/1:1\ CH_2Cl_2–MeCN/41$	−170[l]	*d*	HF/liquid/−80	−195	*m*
HF/HCO_2H/*f*	−180	15	$HF/CFCl_3/34$	−196	*d*
$HF/HCONMe_2/34$	−181	*d*	$HF/MeCO_2H/25$	−217	This work
HF/MeCN/34	−184	*d*		(av. −183)[n]	

[a] System given as: fluoride/solvent/temperature (°C). [b] At infinite dilution unless otherwise indicated. [c] 1 mol dm^{-3}. [d] R. K. Marat and A. F. Janzen, *Can. J. Chem.*, 1977, **55**, 3845. [e] T. C. Waddington, *MTP Int. Rev. Sci., Inorg. Chem. Ser. 1*, 1972, **3**, 101. [f] Probably room temperature. [g] J. Soriano, J. Shamir, A. Netzev, and Y. Marcus, *Inorg. Nucl. Chem. Lett.*, 1969, **5**, 209. [h] J. S. Martin and F. Y. Fujiwara, *Can. J. Chem.*, 1971, **49**, 3071. [i] F. Y. Fujiwara and J. S. Martin, *J. Am. Chem. Soc.*, 1974, **96**, 7625, 7632. [j] L. Gouin, J. Cousseau, and J. A. S. Smith, *J. Chem. Soc., Faraday Trans. 2*, 1977, 1878. [k] Not given. [l] 3 mol dm^{-3}. [m] J. Shamir and A. Netzer, *Can. J. Chem.*, 1973, **51**, 2676. [n] Excluding last value.

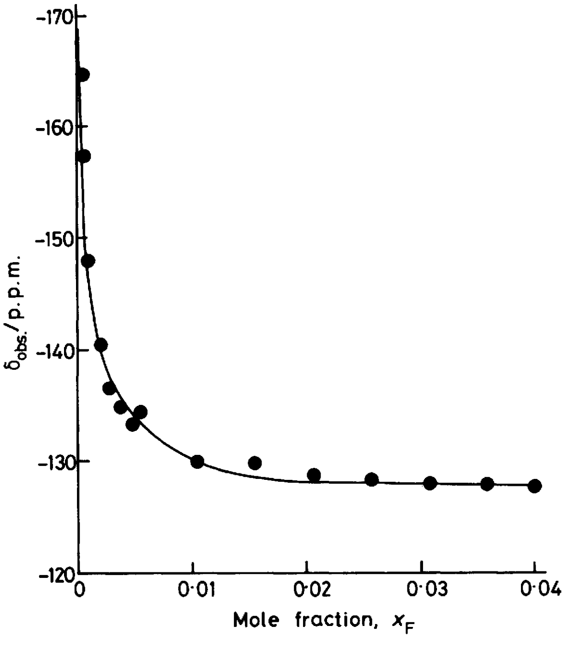

Figure. Variation of $\delta_{obs.}$ of the ^{19}F n.m.r. signal of $NEt_4F–MeCO_2H$ with the mole fraction of fluoride (x_F) at 25 °C

buffered with potassium methanoate. They studied solutions in the concentration range 0.0625—2.00 mol dm^{-3} and in all cases observed one signal in the ^{19}F n.m.r. spectrum which they assumed to be the resultant of the four fluorine environments F^-, HF, HF_2^-, and $(HF)_2$, the acid dimer. Their chemical shifts are shown in Table 2 for F^-, HF, and HF_2^- [$(HF)_2$ was assumed to have the same value as HF].

In a more recent paper Clark and co-workers[18] used ^{19}F n.m.r. spectroscopy to investigate alkali-metal fluorides in diols and carboxylic acids. In these solutions a significant cation effect was expected but not observed. The authors concluded moreover that HF and HF_2^- were unimportant and that the principal fluoride environments were strong hydrogen-bond solvated F^- and ion pairs M^+F^-. With NEt_4F, ion pairing will be much weaker and what we observed was $F(MeCO_2H)_x^-$ at all but the lowest concentrations. It is what happens under high dilution which is revealed in our study.

The most likely upfield entity is some form of protonated fluoride and the equilibrium (1) between them assumes it to be HF_s where s refers to some solvated species. The equilibrium

$$F_s^- + MeCO_2H \xrightarrow{K_c} HF_s + MeCO_2^- \qquad (1)$$

constant (based on concentrations rather than activities) is given by expression (2), and the observed ^{19}F chemical shift, $\delta_{obs.}$, by (3) where *c* is the total concentration of added NEt_4F [see equation (4)]. From equations (2)—(4), relationship (5) can

$$K_c = [HF_s]^2/[F_s^-] \qquad (2)$$

$$\delta_{obs.} = \delta_{F_s^-}[F_s^-]/c + \delta_{HF_s}[HF_s]/c \qquad (3)$$

$$c = [F_s^-] + [HF_s] \qquad (4)$$

$$\delta_{obs.} = \delta_{F_s^-} + (\delta_{HF_s} - \delta_{F_s^-})K_c[(1 + 4c/K_c)^{\frac{1}{2}} - 1]/2c \qquad (5)$$

be deduced. Using the data from Table 1 for $\delta_{obs.}$ and *c*, the three variables $\delta_{F_s^-}$, δ_{HF_s}, and K_c were computed with a general least-squares best-fit program on a model B BBC microcomputer. The values obtained were: $\delta_{F_s^-} = -122.7 \pm 2.1$, $\delta_{HF_s} = -217.4 \pm 58.2$ p.p.m., and $K_c = (1.50 \pm 2.5) \times 10^{-3}$ mol kg^{-1}. The first of these is very much as expected from the Figure. The value for the protonated species, δ_{HF_s}, however needs some explanation since it is well outside the range of values for HF reported in Table 2.

Another relationship that can be derived from equations (2)—(4) is (6), and a plot of $1/(\delta_{obs.} - \delta_{F_s^-})$ *vs.* $(\delta_{obs.} - \delta_{F_s^-})$

$$\frac{1}{(\delta_{obs.} - \delta_{F_s^-})} = \frac{1}{(\delta_{HF_s} - \delta_{F_s^-})} + \frac{(\delta_{obs.} - \delta_{F_s^-})c}{K_c(\delta_{HF_s} - \delta_{F_s^-})^2} \qquad (6)$$

allows δ_{HF_s} to be obtained from the intercept. Such a plot is linear for the lower dilution points and gives $\delta_{HF_s} = -207$ p.p.m. from a least-squares best-line fit ignoring the four highest concentrations.

Clearly in these solutions the species present at low concentrations is not HF, nor $(HF)_2$ as Coulombeau assumed.[15] The sequential change of adding $\frac{1}{2}H^+$ to F^- as shown in (7) points to a species in our solutions that corresponds to $H_{1.5}F^+$ which could be $[HF \cdots H^+ \cdots O_2CMe^-]$.

$$\begin{array}{ccccccc} F_s^- & \xrightarrow[\Delta\delta\, =\, 29]{\frac{1}{2}H^+} & \frac{1}{2}[HF_2]_s^- & \xrightarrow[\Delta\delta\, =\, 30]{\frac{1}{2}H^+} & HF_s & \xrightarrow[\Delta\delta\, =\, 34]{\frac{1}{2}H^+} & H_{1.5}F_s^+ \\ -124 & & -153 & & -183 & & -217 \end{array} \qquad (7)$$

Isotope studies using $MeCO_2D$ showed a 2.8 p.p.m. downfield chemical shift of the ^{19}F n.m.r. signal of NEt_4F in $MeCO_2D$ compared to $MeCO_2H$. This observation is further support for $F(MeCO_2H)_x^-$ being the chief downfield environment, since the effect of deuteriation is to weaken the hydrogen bonding of the solvation sphere, an observation in keeping with a previous study on this system.[10]

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