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DIRECT OBSERVATIONS OF HYDROGEN BONDED FLUORIDE COMPLEXES BY FAST ATOM BOMBARDMENT MASS SPECTROMETRY

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SUMMARY

The direct observation of pre-formed hydrogen bonded fluoride complexes by mass spectrometry has been achieved for the first time by fast atom bombardment of the solid and liquid samples. For a series of substituted phenols hydrogen bonded to fluoride it has been found that the nature of the substituents affect the apparent stability of the complexes as measured by the relative intensities of the ion peaks.

INTRODUCTION

Much of the solution chemistry of the fluoride ion is dominated by hydrogen bonding interactions between F^- and the protic solvent or substrate molecules. These hydrogen bonding interactions are known to result in a loss in local electron density at the fluorine[1,2] causing a reduction in its nucleophilic reactivity[3,4]. Considerable attention has been directed towards the study of hydrogen bonds to fluoride although the direct observation of complexes by mass spectrometric methods has thus far been restricted to species generated in the gas phase via Ion Cyclotron Resonance Mass Spectrometry[5]. Fast Atom Bombardment Mass Spectrometry (FABMS) is a soft ionization technique[6,7,8] requiring no sample heating and might therefore be expected to be suitable for hydrogen bonded complexes which are normally thermally sensitive. In the FABMS technique the sample is subjected to bombardment by 'fast' atoms which brings about desorption and ionisation of the sample. The resulting ions are analysed using conventional mass spectrometric methods and both positive and negative ions can be detected.

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We now report the first successful use of negative ion FABMS for the study of a range of hydrogen bonded complexes of fluoride to phenols.

EXPERIMENTAL

3-Nitrobenzyl alcohol (NBA), 4-nitrophenyloctyl ether (NPOE), tetrabutylammonium fluoride trihydrate (TBAF.$3H_2O$) and all the phenols were obtained from BDH or Aldrich Chemicals. All the above materials used were of standard reagent grade and used without further purification.

Acetonitrile and diethyl ether (Aldrich reagent grade) were dried using activated 4A molecular sieves and sodium wire, respectively, before use.

Negative ion FAB spectra were obtained with a ZAB-E instrument (VG Ltd. Manchester,UK) fitted with a saddle-field FAB gun (Ion Tech, Teddington, UK). Xenon was used as the bombarding atom with a beam energy of ~8 keV. A stainless steel probe tip was used. All spectra were peak averaged from a minimum of 10 scans using an 11/250 data system. FAB samples were prepared by dissolving the complex in a constant amount of matrix liquid, either NBA or NPOE.

The H-bonded complexes were prepared by dissolving 1 mole equivalent of tetrabutylammonium fluoride trihydrate (TBAF.$3H_2O$) in 20 cm^3 of dry acetonitrile to which 2 mole equivalents of the phenol was added. Removal of the bulk of the acetonitrile generally resulted in crystallisation of the complex. Solution ^1H NMR of the complexes in $CDCl_3$ or d_3MeCN showed integration corresponding to a stoichiometric 2:1 (phenol:F^-) complex to be present. Removal of any trace amounts of water was carried out by azeotroping with more dry acetonitrile and washing with dry cold diethyl ether. Finally the complexes were further dried under vacuum (0·1 Torr) and stored at -10°C until required.

RESULTS AND DISCUSSION

Samples for FABMS are generally prepared by dissolving the complex in a suitable matrix liquid such as nitrophenyloctyl ether (NPOE) or 3-nitrobenzyl alcohol (NBA). NBA although capable of complexing with F^-, is useful in cases where the complex is insoluble in NPOE or when the desired peaks coincide with those from the matrix liquid. The use of other solvents such as sulpholane, nitrobenzene, and monothioglycerol is limited by their short lifetimes in the mass spectrometer source. Glycerol is another possible solvent which is commonly used in FABMS but its spectrum shows clustering and it is able to disrupt some of the weaker H-bonded systems.

The negative ion FAB mass spectra of $(ArOH)_2\cdots F^-$ complexes all show peaks due to the $(ArOH)\cdots F^-$, in which one ArOH molecule has been lost from the parent complex. Typically, peaks due to the phenolate anion are also observed along with peaks attributable to the matrix liquid. In a few cases, notably the methylphenol series, we have also observed peaks due to the parent 1:2 complexes. Thus in the case of the (4-methylphenol)$_2$ TBAF complex, the major peaks occur at m/z 266, 251 (Matrix), 235 ($F(HOC_6H_4\text{-}4Me)_2^-$), 138 (Matrix),
127 ($F(HOC_6H_4\text{-}4Me)^-$), 122 (Matrix), and 107 ($4\text{-}MeC_6H_4\text{-}O^-$) (see Fig. 1).

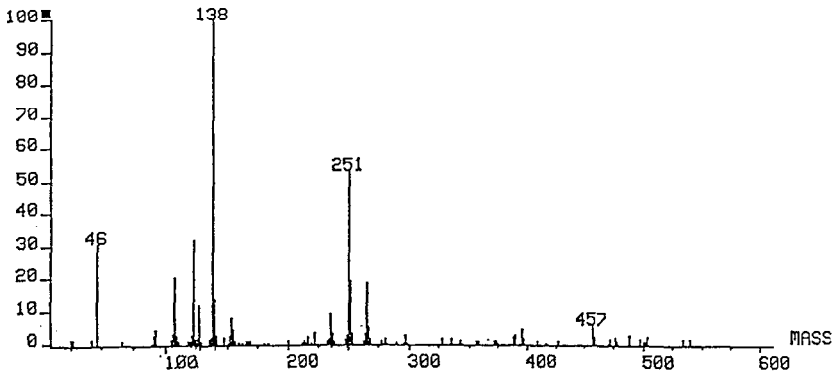

Fig. 1 FAB Spectra of the (4-Methylphenol)$_2$TBAF Complex in NPOE.

When NBA was used as a matrix liquid, an additional peak corresponding to the NBA-F^- hydrogen bonded complex was also observed, at m/z 172

In total, four series of 2,3, and 4- substituted phenols-F^- complexes have been studied. The results are shown in Table 1 in terms of the relative intensities of the phenol-F^- and phenolate anion peaks.

The relative intensities of the 1:1 complex ion peaks for the nitro and cyanophenols can be explained by a combination of electronic and steric effects. The -M groups in the 2- and 4- positions will weaken the complexes by resonance delocalisation of charge

away from the hydrogen bonds. Ortho substituents can also be generally expected to weaken the complex through steric effects. Thus for both series the observed order is 3->4->2-. It is interesting to note that no complex peak is observed in the extreme situation of 2-nitrophenol.

TABLE 1

Ratio of observed 1:1 Complex/Phenolate Peak Intensities for a Series of 2:1 Phenol: F^- H-Bonded Complexes.

Complex	Observed m/z peak for the complex	Peak Intenstity Ratio Complex/Phenolate	Matrix Liquid
(4-Methylphenol)$_2$TBAF	127	0·59	NPOE
(3-Methylphenol)$_2$TBAF	127	0·40	
(2-Methylphenol)$_2$TBAF	127	0·45	
(4-Chlorophenol)$_2$TBAF	147	0.10	NBA
(3-Chlorophenol)$_2$TBAF	147	0.04	
(2-Chlorophenol)$_2$TBAF	147	0·06	
(4-Nitrophenol)$_2$TBAF	158	0·028	NBA
(3-Nitrophenol)$_2$TBAF	158	0·083	
(2-Nitrophenol)$_2$TBAF	158	0·000	
(4-Cyanophenol)$_2$TBAF	138	0·064	NBA
(3-Cyanophenol)$_2$TBAF	138	0·085	
(2-Cyanophenol)$_2$TBAF	138	0·038	

A similar argument using the +M ability of the chloro substituent in the 4- and 2- positions coupled with the steric effect of the 2- substituent can explain the observed order of complex stabilities, 4->2->3-. Interpretation of the methylphenol complex series is less easy although it is interesting to note that all of these complexes have relative stabilities greater than any of the -M substituted phenols and the range of values within the methyl phenol series is very small. Further evidence in favour of the hypothesis of significant steric effects on hydrogen bond complex stabilities can be gained from a study of a series of multiply substituted phenol-F^-complexes of varying substituent

size (Table 2). We have previously shown that these complexes are unusually weak[9] with the 2,6-di-t-butyl-4-methylphenol complex forming a particularly weak hydrogen bond to F^- (so that for example, the complex possesses significant residual nucleophilicity). The FABMS results also reveal a significant steric effect on the relative strength of the hydrogen bond as measured by relative peak intensities.

TABLE 2

Relative Complex Peak Intensities for a Series of Sterically Hindered Phenols Complexed with F^-

Complex†	Observed m/z peak of the complex	Peak Intensity Ratio Complex/Phenolate
(2,4,6-Trimethylphenol)$_2$TBAF	155	0·035
(2,6-Diisopropylphenol)$_2$TBAF	197	0·008
(2,4,6-Tri-t-butylphenol)$_2$TBAF	281	0·005
(2,6-Di-t-butyl-4-methylphenol)$_2$TBAF	-	0·000

† NPOE was used as the matrix liquid in each case.

In conclusion, we have demonstrated that negative ion FABMS is a quick and viable technique for the study of hydrogen bonded F^- complexes. Information relating to the nature and strength of the hydrogen bond is available from the results of such studies.

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