Inhibition of Resonance Delocalisation of Charge by Strong Hydrogen Bonding

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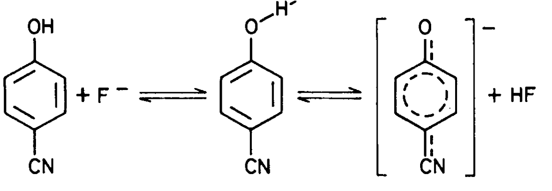
I.r. spectra of solutions containing a 4-cyanophenol–fluoride complex reveal the presence of two distinct types of hydrogen bond between these species and provide evidence for the medium-dependent inhibition of resonance delocalisation of charge by strong hydrogen bonding.

Both *ab initio* calculations[1] and ion cyclotron resonance spectroscopic studies[2] on complexes involving strong hydrogen bonds to fluoride have shown that little resonance delocalisation of charge occurs in such complexes and that the negative charge appears to be largely localised in the three atom XHF^- ($X = O$ or N) hydrogen bond. These conclusions could help to explain the observed selectivity and, in some cases, enhanced reactivity of F^- hydrogen bonded complexes as nucleophiles[3] when compared to their conjugate anions X^-. Unfortunately, it is difficult to correlate results obtained in the gas phase with those obtained in solution especially for interactions involving ions,[2] although spectroscopic evidence has been provided for charge localisation in complex anions hydrogen bonded to hydroxylic solvents.[4] As part of our programme of research into the nature and reactivity of strong hydrogen bonds[3,5,6] we have investigated the properties of the hydrogen bond formed between F^- and 4-cyanophenol. The hydrogen bond assisted alkylation of phenols in the presence of F^- has been shown to be an efficient synthetic method that can be highly selective towards *O*-alkylation of the phenol.[7,8]

Slow evaporation of an aqueous acetonitrile solution containing equimolar amounts of tetra-n-butylammonium fluoride and 4-cyanophenol followed by vacuum drying at 50 °C leaves an anhydrous white solid.† The ^1H n.m.r. spectrum of a solution of this solid in $CDCl_3$ or CD_3CN shows a large downfield shift in the position of the hydroxy proton when compared to the ^1H n.m.r. spectrum of the corresponding solution of the parent phenol [$\Delta\delta(OH) =$ *ca.* 4 p.p.m.]. The i.r. spectrum of the solid shows a broad continuum in the 3000—1000 cm^{-1} region corresponding to the hydrogen bond stretch. These observations are consistent with the presence of a strong $-OHF^-$ hydrogen bond.[9] In a dilute solution of the complex, equilibria involving the free 4-cyanophenol (**1**), the hydrogen bonded 4-cyanophenol (**2**), and the 4-cyanophenoxide anion (**3**) should exist [equation (1)].

We have found that i.r. spectroscopy provides a convenient method of distinguishing between the three species and our results are summarised in Table 1. In all of the solvents investigated, the hydrogen bonded complex (**2**) is the major species. The observed positions of the ν (C≡N) band for (**1**) and (**3**) (Bu_4N^+) are only slightly solvent dependent covering a range of 5 cm^{-1} for (**1**) and 9 cm^{-1} for (**3**) in the solvents used. The difference between the values for the two species is always in the range 30—34 cm^{-1} except for the solid state where ion-pairing will have a major effect (Table 1). The difference between the values for (**1**) and (**2**) is *ca.* 3 cm^{-1} in low polarity solvents and protophobic polar aprotic solvents, whereas it is 14—16 cm^{-1} in the protophilic polar solvents dimethylsulphoxide, *N,N*-dimethylformamide, and *N,N*-dimethylacetamide. On warming solutions of the complex in protophilic polar solvents, the lower energy ν (C≡N) band ($\Delta\nu$ = 14—16 cm^{-1}) is slowly replaced by the higher energy ν (C≡N) band ($\Delta\nu$ = 2 cm^{-1}).‡ The reverse change occurs on cooling the solutions. Solutions of the complex in protophilic polar solvents containing an equimolar (with respect to the complex) or larger than equimolar amount of water also show The lower energy ν (C≡N) band ($\Delta\nu$ = 14—16 cm^{-1}) but the presence of water inhibits any change in the position of the band on heating.



(1)

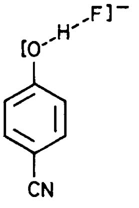
(1) **(2)** **(3)**

The u.v. spectra of solutions of the complex are less informative but do reveal the differences between the complex and the parent phenol or its anion. In acetonitrile for example, the spectrum of the complex is a broad band with λ_{max} *ca.* 270 nm. This value is in between those observed for the phenol (λ_{max} 246 nm) and its anion (λ_{max} 292 nm). Similar results were obtained in dichloromethane but we were unable to obtain useful spectra in the polar protophilic solvents owing to the presence of intense solvent bands in the region of interest.

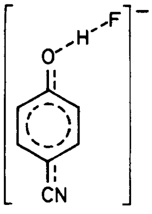
Table 1.

Solvent[a]	$\Delta\nu$(C≡N)/cm^{-1}[b] (**2**)	$\Delta\nu$(C≡N)/cm^{-1}[b] (**3**)
CH_2Cl_2	3	34
$CHCl_3$	4	30
Me_2CO	3	33
C_5H_5N	2	36
MeCN	4	35
Me_2SO	14[c]	34
Me_2NCHO	16[c]	34
Me_2MCOMe	16[c]	36
Solid[d]	22	48

[a] All solutions are 0.13 M. [b] With respect to the value for the free phenol (**1**); 2226 ($CHCl_3$, Me_2CO, and MeCN); 225 (CH_2Cl_2); 2221 (C_5H_5N and Me_2NCHO); 2220 (Me_2SO and Me_2NCOMe); all values to ± 1 cm^{-1}. [c] Along with a shoulder corresponding to the anion, (**3**). [d] KBr discs.



(2a)



(2b)

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† Results from elemental analysis of the product are consistent with an anhydrous 1 : 1 complex of the fluoride and the phenol.

‡ The change in the spectrum occurs slowly in the i.r. beam.

We interpret this solvent-dependent i.r. shift in terms of two possible forms of (**2**), a charge localised form (**2a**) and a charge delocalised form (**2b**). The charge localised form (**2a**) will dominate in the gas phase,[2] and represents a form where the hydrogen bond acts as an electron sink and inhibits resonance. The ν (C≡N) band for (**2a**) should occur at the same energy as that of the neutral molecule, (**1**). In (**2b**) however, resonance will result in a lowering of ν (C≡N) towards the limiting value for the anion (no hydrogen bonding). The proximity of ν (C≡N) for (**2**) to that of (**1**) in all but protophilic polar aprotic solvents strongly suggests that (**2a**) is the dominant form as it is in the gas phase. In the protophilic polar solvents we suggest that (**2b**) is the major form where both the hydrogen bond and the nitrile group help to delocalise the negative charge. A relatively weak band due to the anion (**3**), is also observed in systems containing (**2b**) suggesting that (**2b**) and (**3**) are of similar energy in protophilic polar aprotic solvents. The pK_a of the phenol will be significantly lower in such solvents than in the other solvents investigated[10] and this will favour proton transfer to F^-. No significant band due to (**3**) [or indeed due to (**1**)] is observed in the spectra of solutions containing (**2a**).

Our results show that two quite distinct types of hydrogen bonded complexes between 4-cyanophenol and F^- can exist in solution. The dominant form in most types of solvent shows inhibition of resonance delocalisation of charge comparable to that observed in the gas phase. Localisation of charge within the OHF unit will enhance selectivity of attack towards incoming electrophiles.

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