parison was made between the spectra obtained of these reaction solutions and the spectra of azodicarboxylate esters, those of reaction products (CO_2, N_2O, NO, and the N-tert-butylacetonitrilonium ion), and the absorptions arising from possible contaminants (particularly N_2O_4). Absorptions similar to those that decreased in intensity in $NO^+BF_4^-$ reactions with di-tert-butyl azodicarboxylate were observed in acetonitrile solutions following treatment of diethyl and diphenyl azodicarboxylate with $NO^+BF_4^-$. Due to the apparent low solubility of **4** in nonpolar solvents, comparable absorptions were not detected when the azodicarboxylate esters were added to $NO^+BF_4^-$ in carbon tetrachloride. The reaction between potassium azodicarboxylate with nitrosonium salts was sufficiently rapid at $-15\ ^\circ C$ that infrared spectral analysis of the reaction intermediate could not be made.

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(13) The difference in the standard free energy of formation of N_2O and NO is 4.04 kcal/mol.

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Hydrogen Bonding in Organic Synthesis. 3. Hydrogen Bond Assisted Reactions of Cyclic Organic Hydrogen Bond Electron Acceptors[1] with Halogenoalkanes in the Presence of Potassium Fluoride

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Abstract: The condensation reactions of a number of cyclic organic compounds, benzoic acid, phenol, 1,2-dihydroxybenzene, N-methylaniline, aniline, piperidine, pyrrolidine, phthalimide, and benzene thiol with halogenoalkanes in the presence of potassium fluoride are described. The reactions are thought to be accelerated by the formation of H bonds between the fluoride anion and the cyclic organic electron acceptors. Cesium fluoride in place of KF speeds up the reactions by an order of magnitude. Large shifts in the fundamental stretching vibration of the electron acceptor group have been reported for a number of cyclic organic fluoride systems, indicative of H bonding. Values for the H bond enthalpy of selected systems fluoride–benzoic acid, fluoride–phenol, and fluoride–1,2-dihydroxybenzene (113 ± 5, 60 ± 5, and 63 ± 7 kJ mol^{-1}, respectively) have been predicted on the basis of reported correlations between the H bond enthalpy and the IR shift on H bonding.

The importance of using ionic salts in organic synthesis has been recognized for many years. One of the apparent drawbacks with such applications is that most solvents capable of dissolving both the ionic salt and organic reactants are protic solvents and through H bonding tend to solvate anions particularly strongly, and anions, as bases and nucleophiles, are usually the important half of an ionic reagent. Alkali metal fluorides fall into this category and efforts to apply these salts to organofluorinations have often met with little success. Although it has been recognized that the ineffectiveness of many

alkali metal fluoride-solvent systems as fluorinating agents is partly due to anion-solvent interaction, there have been no deliberate attempts to follow this up.

The first time that the base behavior of KF was recognized was when Nesmayanov observed that the reaction of KF and trichloroacetic acid yielded chloroform and carbon dioxide instead of the expected fluorocarboxylic acid products.[2] Since that time, a number of workers have reported unexpected reactions occurring in the presence of KF[3] or have actually reported the function of KF as a base.[4-6] Maynard, in his studies[3] with KF in high boiling point polar aprotic solvents such as N,N-dimethylformamide and N-methylpyrrolidin-2-one as agents for the fluorination of highly chlorinated materials, noted that in some cases complex reactions occurred in which very different products to those of the starting material were obtained. Rand reported the apparent function of KF as a base in the Hofmann reaction[4] and in the Knoevenagel reaction[5] and concluded that KF appeared to act as a base even in nonpolar media.[6]

More recently, interest in KF as a potential base in organic chemistry has been revived by the advent of crown ethers, which are capable of dissolving many organic salts including fluorides by cation solvation. The solubilization of KF by 1,4,7,10,13,16-hexaoxacyclooctadecane (18-Crown-6) in benzene and displacement and elimination reactions of the "naked" fluoride with halogen-carrying aliphatics and aromatics have been reported.[7] There has also been a considerable amount of interest in the last few years in tetraalkylammonium fluorides, which have been used more and more for different purposes in preparative organic chemistry, for example, for the cleavage of *tert*-butyl dimethylsilyl ether[8] or for the synthesis of hydantoins.[9]

As a result of the discovery that alkali metal fluorides are very soluble in acetic acid,[10] studies on these and related systems have revealed the presence of very strong H bonds between the acid hydroxyl and the fluoride anion[11-13] comparable in strength to that in the bifluoride anion. Fluoride-acetic acid systems proved to be extremely efficient acetoxylating agents, but only mild fluorinating agents.[14] At first glance, it might appear that this is another example of fluoride functioning as a base; however, it is more realistic to differentiate this situation from the role of purely a proton acceptor. Instead, the fluoride anion may be considered as a source of electrons which acts, via the H bond, to transfer negative charge to the organic part of the complex, hence generating a highly reactive acetoxy anion.

The efficiency of the KF-acetic acid system as an acetoxylating agent led us to investigate the possibility of imitating this mechanism for a number of other organic molecules capable of acting as H bond electron acceptors. Early results of our efforts in this field were most encouraging and were reported in a preliminary communication.[15] This paper describes the reactions of KF and a number of selected aromatic and cyclic organic compounds capable of acting as H bond electron acceptors with halogenoalkanes. The reactions are usually more rapid and provide higher recoverable yields than standard methods for the preparation of the various condensation products. Infrared studies on selected systems have confirmed the presence of H bonds between the fluoride anion and the organic molecule which serve to direct negative charge toward the organic part of the complex.

Experimental Section

Instrumentation. The NMR spectra were recorded on Varian A-60 or Brüker WP-60FT (60 MHz) spectrometers. IR spectra were recorded on Perkin-Elmer 237B or Perkin-Elmer 225 spectrometers. Mass spectra were obtained on an AEI MS-30 double-beam mass spectrometer using both the direct probe and interfaced (Watson-Bieman) GC as inlets.

Materials. Metal fluorides were commercial samples dried at 100 °C in vacuo for several hours. Tetramethylammonium chloride was a commercial sample dried at 100 °C in vacuo for 2 h. Tetrabutyl- and tetraethylammonium fluorides were prepared in aqueous solution by neutralization of the hydroxides (commercial samples in aqueous solution) with 52% hydrofluoric acid. The mixtures of the quaternary ammonium fluorides with benzoic acid, phenol, 1,2-dihydroxybenzene, phthalimide, and benzene thiol were prepared by evaporating mixtures of the concentrated solution of the fluoride in water and excess of the organic acceptor in ethanol at 90 °C in vacuo until the IR and/or ^{1}H NMR showed no water remaining. In the absence of the organic electron acceptor, it was found to be quite impossible to remove all of the water under these conditions. The purity of these mixtures was checked by ^{1}H NMR spectroscopy using $CDCl_3$ solutions in which all of the samples were reasonably soluble. Under these conditions there is no evidence for splitting of the H-bonded proton due to coupling with ^{19}F, although some broadening and marked downfield shifts were observed. Some changes in the nature of the ring C-H proton resonances were, however, noted; these may be attributable to long-range [1]H-^{19}F coupling. Samples of the monosolvates of KF and CsF with benzoic acid, phenol, and 1,2-dihydroxybenzene (mono- and hemisolvates) were also prepared by fusing together the solids at a little above the melting points of the organics. All $\Delta\nu_s(AH)$ shifts for a particular organic substrate agreed to within ±50 cm^{-1}.

Analytical grade N,N-dimethylformamide was dried over molecular sieves as was analytical grade acetic acid. All the organic electron acceptors were commercial materials, freshly distilled when used with the exceptions of benzoic acid, 1,2-dihydroxybenzene, and phthalimide, which were used as obtained. The halogenoalkanes were used as commercially obtained. All ^{1}H NMR spectra were recorded in $CDCl_3$ solution with $\simeq$1% v/v tetramethylsilane as internal reference.

Reactions. Reactions were monitored by sampling and ^{1}H NMR analysis. In most of the reactions described, the reaction was stopped after ^{1}H NMR monitoring showed 100% conversion, confirmed by extracting the inorganic salts either by filtration or by aqueous extraction and determining the halide content via a AgX determination. Products were generally isolated by standard (work-up) procedures and identified by routine analysis and, where possible, by comparison to authentic samples. Reaction details for the various condensations that were attempted are summarized and, where possible, compared to standard preparation procedures in Table I. Experimental details for one representative preparation are given below.
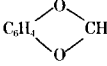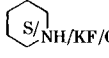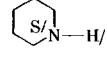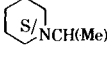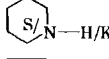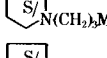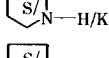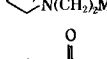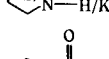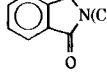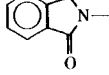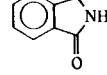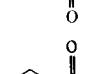
1,4-Dichlorobutane and KF in Benzoic Acid. 1,4-Dichlorobutane (2.54 g, 0.02 mol) was heated with a molten mixture of KF (5.81 g, 0.1 mol) in benzoic acid (48.8 g, 0.4 mol) at 130 °C. After 1.5 h (100% reaction by ^{1}H NMR), the reaction mixture was cooled, extracted with diethyl ether, and the acid neutralized with bicarbonate. Drying ($MgSO_4$), evaporation, and recrystallization from EtOH gave 1,4-dibenzoxybutane (5.4 g, 0.018 mol, 90%): mp 79 °C (lit.[16] 80 °C); ^{1}H resonances at δ 8.02 (m, 4 H, ring C-H), 7.85 (m, 6 H, ring C-H), 4.36 (t, 4 H, CH_2), and 1.92 (m, 4 H, CH_2); m/e 298. When the reaction was carried out in DMF (100 g) as solvent at 130 °C, ^{1}H NMR monitoring showed 100% reaction (88% recoverable) after 1.5 h.

Results

The H bond assisted condensation reactions that have been attempted between cyclic organic electron acceptors and halogenoalkanes in the presence of KF are summarized and, where possible, compared to standard preparations in Table I. It should be emphasized that the reactants chosen serve only as examples meant to illustrate O-H, N-H, and S-H groups acting as H bond electron acceptors. There is no reason to suppose that many other solvents and halogen-carrying aliphatics would not behave in a similar manner.
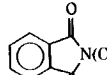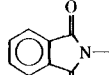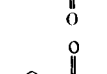
Benzoic acid, phenol, 1,2-dihydroxybenzene, N-methylaniline, aniline, pyrrolidine, piperidine, phthalimide, and benzene thiol all undergo efficient condensation reactions with halogenalkanes in the presence of KF. The reactions are usually more rapid and provide higher recoverable yields than standard methods for the preparation of the various condensation products (see Table I). In most of these reactions, the avoidance of a solvent and the overall efficiency of the reaction

500

Table 1. Preparation of Various Organic Condensation Products by Standard and H Bond Assisted Reactions

	H bond assisted preparation						Standard preparation				
Desired product	Starting materials	Solvent	Time, h	% Reaction by ¹H NMR	Recoverable yield %	Temp, °C	Starting materials	Time, h	Yield, %	Temp, °C	Ref
$PhCO_2(CH_2)_4O_2CPh$	$PhCO_2H/KF/Cl(CH_2)_4Cl$		1.5	100	90	130					
$PhCO_2(CH_2)_4O_2CPh$	$PhCO_2H/KF/Br(CH_2)_4Br$		0.25	100	85	130	$PhCO_2K/Br(CH_2)_4Br/DMF$	1	80	140	a
$PhCO_2(CH_2)_4O_2CPh$	$PhCO_2H/KF/Br(CH_2)_4Br$	DMF	0.5	100		130					
$PhCO_2(CH_2)_4O_2CPh$	$PhCO_2H/KF/Br(CH_2)_4Br$	MeOH	3	12							
$CH_3CH(O_2CPh)CO_2H$	$PhCO_2H/KF/CH_3CH(Cl)CO_2H$		0.5	100	90	130	$PhCO_2H/CH_3CH(Cl)CO_2H$	6	20	130	a
$PhCO_2CH_2CH_2Me$	$PhCO_2H/KF/Me(CH_2)_2Cl$		1.5	100	95	120					
$PhO(CH_2)_4OPh$	$PhOH/KF/Br(CH_2)_4Br$		0.5	100	93	120	$PhOH/NaOH/Cl(CH_2)_4Cl$	1	49	150	38
$CH_3CH(OPh)CO_2H$ or $CH_3CH(OC_6H_4R)CO_2H$	$PhOH/KF/CH_3CH(Cl)CO_2H$		0.1	100	95	120	$R\text{-}C_6H_4OH/CH_3CH(Cl)CO_2Na$	8	≈30		39
C_6H_4 (methylenedioxy) CH_2	$C_6H_4(OH)_2/KF/CH_2Br_2$	DMF	1	100	85	120	$C_6H_4(OH)_2/CH_2Cl_2/NaOH/H_2O/EtOH$	15–18	23.2	110	19
$PhN(Me)(CH_2)_4N(Me)Ph$ or $PhN(Me)(CH_2)_5N(Me)Ph$	$PhN(Me)H/KF/Cl(CH_2)_4Cl$		1		20	130	$PhN(Me)H/Na_2CO_3/Br(CH_2)_5Br\cdot$	24	22	105	17
$PhN(C_4H_8)$ᵇ			1		36	130	$PhNH_2/Cl(CH_2)_4Cl$	4		100	40
$PhNMe_2$			1		37	130					
$PhN(Me)(CH_2)_2N(Me)Ph$	$PhN(Me)H/KF/Cl(CH_2)_2Cl$		6	100	92	110	$PhN(Me)H/Na_2CO_3/Br(CH_2)_2Br$	24	83	105	41
$PhN(H)(CH_2)_3Me$	$PhNH_2/KF/Cl(CH_2)_3Me$		2	100	70	110	$PhNH_2/BuBr/ZnCl_2/H_2O$	5	75	100	42
$PhN(C_4H_8)$ᵇ	$PhNH_2/KF/Br(CH_2)_4Br$		0.25	100	92	120	$PhNH_2/Cl(CH_2)_4Cl$	4		100	40
thiazoline-$N(CH_2)_3Me$	thiazoline-$NH/KF/Cl(CH_2)_3Me$		1	100	80	100	thiazoline-$N\!-\!H/Br(CH_2)_3Me/KOH/H_2O$	1+	70–80	100+	43
thiazoline-$NCH(Me)CH_2Me$	thiazoline-$N\!-\!H/KF/MeCH(I)CH_2Me$		0.5	100	86	100					
pyrroline-$N(CH_2)_3Me$	pyrroline-$N\!-\!H/KF/Cl(CH_2)_3Me$		1	100	93	80	$BuNH_2/(CH_2CH_2Cl)_2/K_2CO_3/EtOH$	60	52	100	44
pyrroline-$N(CH_2)_2Me$	pyrroline-$N\!-\!H/KF/Cl(CH_2)_2Me$		1	100	94	80	$PrI + K$ pyrrolate			100	45
phthalimide-$N(CH_2)_2Me$	phthalimide-$N\!-\!H/KF/Cl(CH_2)_2Me$	DMF	4	100	73	110	phthalimide-$NH/K_2CO_3/Cl(CH_2)_4Me$	2+	45	130	a
phthalimide-$N(CH_2)_3Me$	phthalimide-$N\!-\!H/KF/Cl(CH_2)_3Me$	DMF	2	100	92	120					
phthalimide-$N(CH_2)_5Me$	phthalimide-$N\!-\!H/KF/Cl(CH_2)_5Me$	DMF	2	100	97	120					
$PhS(CH_2)_4SPh$	$PhSH/KF/Cl(CH_2)_4Cl$		4	100	92	130					
$MeCH(SPh)CH_2Me$	$PhSH/KF/MeCH(I)CH_2Me$		8	100	92	130	$PhSNa/CH_3CH(Br)CH_2Me$	24	45	110–120	46

ᵃThis work. ᵇNC_4H_8, pyrrolidinyl.

facilitates separation procedures and helps to afford high recoverable yields. The inorganic components may be removed in the aqueous extract or by filtration and any excess of unreacted aromatic may be readily removed by chemical methods or by distillation.

The reactions described generally produced the simple condensation product only, no side reactions such as the production of fluoroalkane were evident, although the introduction of a protic solvent such as methanol to the system may lead to competing solvolysis reactions should this solvent be capable of successfully competing with the cyclic organic for the fluoride anion (see later). In the reaction of 1,4-dihalogenobutane with a mixture of KF and N-methylaniline, three products were found in the final reaction mixture: N,N'-dimethyl-N,N'-diphenyl-1,4-tetramethylenediamine (the expected condensation product), N,N'-dimethylaniline, and N-phenylpyrrolidine in the approximate mole ratio 1:2:2. The predominance of the latter two products is probably due to preferred cyclization as was suggested earlier in an attempt to prepare compounds of the type PhN(Me)(CH$_2$)$_n$N(Me)-Ph.[17]

Apart from the potential application of the method of H bonding assisted synthetic reactions both in general and to condensations in particular, there are a number of individual reactions described that are of special interest and merit individual attention. The methylenation of 1,2-dihydroxy compounds is of particular importance in the synthesis of methylenedioxy-carrying alkaloids. Present methods for the introduction of the methylene group into these compounds are tedious, often inefficient, and require the use of strong base, which is often undesirable, especially where the reactant molecule contains other base-sensitive groups. Previous attempts to prepare benzo-1,3-dioxole, for example, have, until recently, met with little success. The use of metal hydroxide for periods of 15-72 h at temperatures around 100 °C have provided yields of 20-26%.[18,19] More recently, the use of dimethyl sulfoxide as solvent has improved the yield to 91%;[20] however, this is a tedious preparation involving a nitrogen atmosphere and successive additions of 1,2-dihydroxybenzene and sodium hydroxide over a period of some 4 h. The KF/DMF method appears to offer a remarkably efficient, simple, and inexpensive route to such condensations. The reaction of 1,2-dihydroxybenzene and dibromomethane in KF/DMF produces greater than 80% benzo-1,3-dioxole in 1 h.[21]

The preparation of N-alkylphthalimides is of special significance because these compounds are intermediates in the Gabriel synthesis of pure amines.[22,23] Original attempts to synthesize these compounds usually required treating the alkyl halide with potassium phthalimide together at temperatures in the range 120-140 °C for periods of up to several hours even though such conditions were recognized as undesirable and sometimes dangerous.[24] The introduction of an aprotic solvent such as DMF considerably reduced the time required for such condensations,[25] although there is still room for improvement. Our method offers an obvious alternative to standard procedures involving the direct use of potassium phthalimide or phthalimide plus base. Although KF is only marginally more efficient than potassium carbonate, CsF is an extremely vigorous reagent for these condensations (see Table II).

The effect of varying the metal cation on the reaction of alkali metal fluorides with phthalimide and halogenoalkanes in DMF is summarized in Table II. Lithium and sodium fluorides show no appreciable reaction under conditions for which potassium, rubidium, and cesium fluorides are effective. This is in accordance with other attempts to measure the relative reactivity of alkali metal fluorides in organofluorination reactions.[26] The dramatic decrease in the time required for 100% reaction on going from KF to CsF is particularly noteworthy. Such large differences on varying the metal cation are

Table II. The Effect of Varying the Cation on the Reaction of Alkali Metal Fluoride with Phthalimide and Halogenoalkanes in DMF

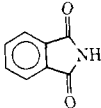|		Preparation of N-alkyl phthalimide			
Fluoride	Halogenoalkane	Time, h	% reaction by ^{1}H NMR	Yield, %	Temp, °C
LiF	Me(CH$_2$)$_2$Cl	10	<1		110
NaF	Me(CH$_2$)$_2$Cl	10	<5	2	110
KF	Me(CH$_2$)$_2$Cl	4	100	73	110
RbF	Me(CH$_2$)$_2$Cl	1	100	82	110
CsF	Me(CH$_2$)$_2$Cl	<0.2	100	82	110
KF	Me(CH$_2$)$_3$Cl	2	100	92	120
CsF	Me(CH$_2$)$_3$Cl	<0.2	100	84	120
KF	Me(CH$_2$)$_5$Cl	2	100	97	120
CsF	Me(CH$_2$)$_5$Cl	<0.2	100	92	120

not apparent in alkali metal fluoride organofluorinations.[26] This may be explained by considering the condensations as requiring the formation of an ion pair of the type M$^+$[F···solvent]$^-$ preceding the reaction—should this be the case, the use of cesium fluoride would enhance the rate of reaction, especially where the solvent is particularly large as in the case of phthalimide. These marked variations in rate on changing the metal cation might not be expected in cases where the solvent is quite small and this was found to be the case in acetoxylations involving MF/acetic acid.[27]

Manifestations of H Bonding between Fluoride and the Cyclic Organic Electron Acceptor. It is well established that the formation of an H bond in a solution or compound modifies a great many physical properties. The most important, or most commonly observed physical property modifications are frequency shifts of IR and Raman bands, altered freezing and boiling points, solubility differences resulting from H bonding between solute and solvent, changed electrical conductivities, and proton magnetic resonance shifts. In an attempt to show, beyond reasonable doubt, that H bonding occurs between fluoride and the protic organics used in this work, it was decided to concentrate on frequency shifts in the IR resulting from H bonding between fluoride and selected solvents. However, other physical property modifications on H bond formation in some of these systems are also apparent. For example, KF is quite soluble in molten phenol, benzoic acid, and 1,2-dihydroxybenzene and solutions of quaternary ammonium fluorides in the above and in benzene thiol show appreciable downfield shifts in the magnetic resonance of the H bonding protons.

The most prominent of the spectral changes on H bond formation occurs in the fundamental stretching vibration of the electron acceptor hydrogen group (ν_s(AH)). These changes have attracted the most attention in assuming qualitative criteria for H bond formation and for determining actual H bond energies. A number of correlations between these changes and the H bond enthalpy have been proposed and we have determined to use some of these correlations for predicting the H bond enthalpies of a few of our systems.

Apart from the hydrogen bifluoride anion, few anionic H bonds have been investigated.[12,13,28-31] However, it has become established that anionic H bonds are often unusually strong[12,13,30] and provide large changes in ν_s(AH).[12,13,29] A direct correlation between $\Delta\nu_s$(AH) and the $\Delta H°$ of some anionic H bonds has already been applied with apparent success.[12,13] The $\Delta\nu_s$(AH) values observed for the selected systems fluoride-phenol, fluoride-benzoic acid, fluoride-1,2-dihydroxybenzene, fluoride-phthalimide, and fluoride-benzene thiol are given along with observed ν_s(AH) values for the "free" solvent monomers and the $\Delta\nu_s$(AH) values for the self-association of the solvents in Table III. In addition to these, values for the H bond length, r(OHF), and for the H bond enthalpy based on a maximum of three reported $\Delta\nu_s$-$\Delta H°$ correlations[13,32,33] for the first three of these systems are given in this

Table III.

H bond electron acceptor (AH)	Monomer AH $\nu_s(AH)$,[a] cm⁻¹ ± 5	Dimer (AH)₂				[A–H...F]⁻					
		$\nu_s(AH)$,[a] cm⁻¹	$\Delta\nu_s$,[a] cm⁻¹	r(AHA),[a] Å ± 0.01	−ΔH°, kJ mol⁻¹	$\nu_s(AH)$,[a,b] cm⁻¹	$\Delta\nu_s$,[a] cm⁻¹	r(AHF̄),[a] Å ± 0.01	−ΔH°,[a] kJ mol⁻¹	−ΔH°,[a] kJ mol⁻¹	−ΔH°,[a] kJ mol⁻¹
PhCO₂H[c]	3540[d]	3000 ± 50	540 ± 55	2.64	33.8[e]	1500 ± 100	2040 ± 105	2.42		114 ± 1	113 ± 5
PhOH[c]	3620[d]	3330 ± 20	290 ± 25	2.80	21.3[f]	2550 ± 50	1070 ± 55	2.55	60 ± 4	64.5 ± 0.5	59 ± 4
C₆H₄(OH)₂[c]	3620[d]	3330 ± 20	290 ± 25	2.80	21.3[g]	2500 ± 100	1120 ± 105	2.54	63 ± 5	65.0 ± 0.5	62 ± 6[h]
(structure) NH	3545	3185 ± 20	360 ± 25			2970 ± 80	575 ± 85				
PhSH	2585[d]	2564 ± 5	21 ± 10			2310 ± 20	275 ± 25				

[a] This work. [b] All ν_s(AH ... F̄) bands are very strong and very broad. [c] The differences in the melting points between the organics and the KF monosolvates were found to correlate remarkably well with calculated ΔH° values, viz., Δ(PhCO₂H) = 113 ± 5; Δ(PhOH) = 53 ± 2; and Δ(C₆H₄(OH)₂) = 60 ± 2 °C. [d] 0.002–0.005 M solutions in cyclohexane. [e] Reference 47. [f] Reference 48. [g] Assume Δν_s is directly proportional to ΔH°(PhOH)₂ = ΔH°(C₆H₄(OH)₂)₂. [h] Assume ΔI(phenol) = ΔI(C₆H₄(OH)₂) = 8.50 V, see text.

table. Each of these series of calculated values will be discussed in turn.

(a) The H Bond Length, r(OHF̄). Correlations between $\Delta\nu_s(AH)$ and the A···B distance in A–H···B H bonds are well known. The values of $r(OHF̄)$ for the systems fluoride–benzoic acid, fluoride–phenol, and phenol–1,2-dihydroxybenzene and for the self-associated organic systems have been calculated by the use of Bellamy and Owen's empirical relationship between $\Delta\nu_s(AH)$ and the A–H···B distance[34]

$$\Delta\nu_s(\text{cm}^{-1}) = 50[(d/R)^{12} - (d/R)^6] \qquad (1)$$

The relationship is based on the importance of van der Waals repulsions between the nonbonding orbitals of A and B atoms. This method has already been applied to the very strong anionic H bonds formed between carboxylate and fluoride with carboxylic acids.[35] The value for $d(OHF)$ is taken to be 3.30 Å,[35] which is close to the sum of the collision radii of O and F.[34] The short bond lengths calculated for the O–H···F̄ anionic H bonds are in accordance with the proposition that we are dealing with strong to very strong H bonds.

(b) $\Delta\nu_s(AH)$–$\Delta H°$ Correlation for Phenols. The first column of calculated $\Delta H°$ values for the anionic O–H···F̄ H bonds gives values for phenol–fluoride and 1,2-dihydroxybenzene–fluoride based on the $\Delta\nu_s(AH)$–$\Delta H°$ relationship for phenols derived by Drago and Epley[32]

$$-\Delta H(\pm 0.2) = 0.0105\Delta\nu_s + 3.0 \text{ (kcal mol}^{-1}) \qquad (2)$$

This equation is based on a least-squares plot of the values of $\Delta\nu_s(OH)$ vs. the calorimetrically determined $\Delta H°$ values of adduct formation for a series of bases with phenol. Although the original correlation was based on neutral H bonds of $-\Delta H°$ up to 10 kcal mol⁻¹, it is assumed for our purposes that it may be extended to somewhat stronger anionic H bonds. The lack of $\Delta\nu_s$–$\Delta H°$ correlations available for dihydroxybenzenes has led us to further extend Drago and Epley's relationship to 1,2-dihydroxybenzene.

(c) Relationship between $\Delta H°$ and the H Bond Length. The second column of calculated $\Delta H°$ values for the anionic H bonds fluoride–benzoic acid, fluoride–phenol, and fluoride–1,2-dihydroxybenzene are based on Allen's relationship for the determination of the dissociation energy of strong anionic H bonds[33]

$$E_D(AH\bar{B}) = E_D(AH)_2 R_{AA}(\Delta I_{\bar{B}}/R_{AH\bar{B}})\Delta I_{AH} \qquad (3)$$

where $E_D(AH\bar{B})$ is the dissociation energy of the H bond, $E_D(AH)_2$ the dissociation energy of the self-associated electron

acceptor, R_{AA} the internuclear separation in the self-associated electron acceptor, $\Delta I_{\bar{B}}$ the difference between the first ionization potential of the electron donor and that of the noble gas atom in its row, $R_{AH\bar{B}}$ the H bond length, and ΔI_{AH} the difference between the first ionization potential of the electron acceptor and that of the noble gas atom in its row. For the purpose of our calculations, $E_D(AH)_2$ values are shown in Table III ($E_D(AHB)$ is taken to equal $-\Delta H°(AHB)$ for the purpose of our calculations and comparisons); E_D-$(C_6H_4(OH)_2)_2$ is taken to be equal to that of phenol;[36] R_{AA} and $R_{AH\bar{B}}$ values are shown in Table III and are based on Bellamy and Owen's relationship between $\Delta\nu_s$ and the H bond length;[34] $I_{\bar{F}}$, I_{neon}, and I_{AH} values are taken from the literature except for $I(C_6H_4(OH)_2)$, which is taken to be equal to that of phenol. Allen found that direct predictions of the dissociation energies of the (FHF)⁻ and (FH₂O)⁻ H bonds using eq 3 gave values approximating to 50% of the experimentally determined values.[33] We checked this discrepancy by using eq 3 to predict the dissociation energy of the very strong H bond (F̄···HOAc)⁻, the experimental $\Delta H°$ value of which is known[11] and has been verified by $\Delta\nu_s$–$\Delta H°$ correlations.[13] We found that Allen's relationship predicted $E_D(FHOAc)⁻$ = 65 kJ mol⁻¹ compared to the known $\Delta H°(FHOAc)⁻$ of −120 kJ mol⁻¹—further evidence for Allen's observation that his predicted values fall close to 50% of the "known" values. Allen explained this discrepancy in terms of the failure of his correlation to take into account the Coulomb interaction between F̄ and the slightly positive hydrogen and the additional charge polarization of the electron acceptor also produced by F̄. Our calculated values shown in Table III correspond to twice the values calculated using eq 3.

(d) Direct Correlation between $\Delta\nu_s(AH)$ and $\Delta H°$ for Anionic H Bonds. The values for $-\Delta H°(OH···F)⁻$ quoted in the final column of Table III are based on Clark and Emsley's direct $\Delta\nu_s(OH)$–$\Delta H°$ conversion factor of:

$$[\Delta\nu_s(OH)/\Delta H°] = -18 \text{ cm}^{-1} \text{ kJ}^{-1} \qquad (4)$$

calculated on the basis of known $\Delta\nu_s$ and $\Delta H°$ values for the (FHO₂CMe)⁻ and (MeCO₂H)₂ H bonds.[13] This relationship led to meaningful results with other anionic H bonds.[12,13]

All of the calculated $\Delta H°$ values for the (OH···F)⁻ H bonds are based on direct or indirect correlations with $\Delta\nu_s(OH)$. While it is recognized that IR shifts give only approximate values of $\Delta H°$, and that for some systems agreement between $\Delta\nu_s$ and $\Delta H°$ is virtually nonexistent, in our case we feel that the similarity in the type of H bond we have focused on allows

us to use such methods with some degree of confidence. Inspection of the calculated values goes a long way to supporting our view. Direct correlations between values such as $\Delta\nu_s(AH)$ and $\Delta H°$ eliminate the need for tedious calorimetric determinations of the enthalpies of adduct formation; indeed such determinations are often very difficult because of the nature of particular solvent–solute systems such as in our case. However, although the limitations of indirect $\Delta H°$ determinations should be appreciated, truly accurate results cannot be expected and we believe that at least two independent correlations should be tried wherever possible before predicted $\Delta H°$ values can be regarded with a reasonable amount of confidence.

The calculated $\Delta H°$ values for the three $(OH\cdots F)^-$ systems investigated here suggest the presence of strong H bonds, outside the traditionally "normal" range of H bond enthalpies, i.e., $\simeq 8–40$ kJ mol^{-1}. The calculated value for fluoride–benzoic acid (113 ± 5 kJ mol^{-1}) is very close to those determined for fluoride–acetic acid[11] and fluoride–trifluoroacetic acid,[13] as might be expected. The calculated value for fluoride–phenol (60 ± 5 kJ mol^{-1}) actually falls below that determined for the chloride–phenol H bond (72 ± 5 kJ mol^{-1}),[30] which is rather surprising when one considers that the fluoride anion is generally thought to be a far better H bond electron donor than chloride. Indeed the same authors found values of 58 ± 3 and 71 ± 3 kJ mol^{-1} for the chloride–acetic acid and chloride–trifluoroacetic acid H bonds, well below those determined for the fluoride analogues (120 ± 6 and 113 ± 6 kJ mol^{-1}, respectively),[11,13] as would be expected. We have measured $\nu_s(OH\cdots Cl)^-$ shifts of 3170 ± 50 and 2600 ± 50 cm^{-1} for chloride (Me$_4$NCl) with phenol and acetic acid, respectively, which represent $\Delta\nu_s$ values of 450 ± 55 and 1020 ± 55 cm^{-1}.[37] If we substitute these values into eq 2 and 4, respectively, we obtain predicted values for $\Delta H°$ of 32 ± 3 (PhOH$\cdots$Cl)$^-$ and 57 ± 3 kJ mol^{-1} (MeCO$_2$H$\cdots$Cl)$^-$. The latter value corresponds very closely to that obtained previously[30] and both values come very close to equalling 50% of the values for the fluoride analogues. This suggests that Lam et al.[30] may be in error for their chloride–phenol H bond, though all their other data is consistent with ours.

While we have not attempted to determine any thermodynamic data for other adducts described in this work, it should be reasonable to assume on the basis of the observed frequency shifts and the similarity of the other systems that we are also dealing with anionic H bonding, probably moderate to strong in nature, certainly stronger than any neutral H bonds of the various electron acceptors. For example, the observed $\Delta\nu_s(SH)$ of 275 ± 25 cm^{-1} is, to the best of our knowledge, by far the largest shift that has been observed for H bonds involving benzene thiol as the electron acceptor.

We plan to carry out further investigations into this field, particularly with regard to ^{1}H and ^{19}F NMR investigations on fluoride–protic organic solvent systems in an attempt to provide further evidence for and information on the H bonds formed therein.

Discussion

Although the use of metallic fluorides in organic synthesis has caused some surprises in the past, it is quite remarkable, from a conventional viewpoint, that KF should function so efficiently in the reactions described in this work. In order to consider the nature of these reactions and the possible general significance of H bonding in synthesis, it is necessary to first establish the role of the fluoride anion.

The fluoride is not a catalyst nor does it function effectively when present in catalytic amounts. The inorganic side products in all of these reactions are the potassium salt of the displaced halogen and potassium hydrogen bifluoride; the minimum amount of KF required is the calculated amount necessary to provide quantitative yields of these materials. In practice an excess of KF is preferred. It is unlikely that these reactions involve an initial proton-transfer mechanism, i.e., $\bar{F} + AH \rightarrow \bar{A} + FH$; there is no evidence for the existence of HF or of HF$_2^-$ in solutions of fluorides in the protic organics, even at high temperatures. The role of the fluoride is to provide a highly reactive solvent anion by H bonding to the most acidic proton of the organic molecule. In solutions of fluoride in carboxylic acids, the H bond formed between the fluoride anion and the hydroxyl proton is very strong (110–120 kJ mol^{-1}),[11-13] indeed stronger than some of the weaker covalent bonds. It is therefore perhaps not very surprising that such systems behave in an expected manner on treatment with a halogen-carrying aliphatic.[14] In this work, a number of other hydroxylic electron acceptors have been investigated—benzoic acid, phenol, and 1,2-dihydroxybenzene. In each case, the H bond formed with $\bar{F}$ may be classed as strong or very strong and it is not very surprising that these systems should behave in a manner similar to fluoride–carboxylic acid systems. However, on extending the range of electron acceptors to amines and thiols, we are no longer dealing with conventionally strong H bond electron acceptors and, although anionic H bonds of the type $(N-H\cdots F)^-$ and $(S-H\cdots F)^-$ should be stronger than neutral N–H or S–H H bonds, one cannot expect them to be close in strength to those involving O–H as the electron acceptor group. Despite this, amine–KF and thiol–KF systems are very good sources of the solvent anions, far more so than any conventional picture of KF behaving purely as a base could predict. It must be assumed, therefore, that even these weaker anionic H bonds are of considerable importance in dictating the rate and efficiency of subsequent reactions.

That the fluoride anion is effectively masked as an effective nucleophile on mixing with a protic solvent is readily apparent by the total lack of any fluoroalkane products found in the reaction mixtures. However, when a protic solvent is absent and an aprotic solvent such as DMF is used, fluorination and/or dehydrohalogenation processes may occur; indeed it is only through the use of dipolar aprotic solvents such as DMF that a number of organofluorinations (and efficient dehydrohalogenations) have been achieved with alkali metal fluorides. Short-chain halogenalkanes such as 1,4-dihalogenobutane will undergo, often fairly rapid, fluorination and/or dehydrohalogenation on heating with KF/DMF; however, should the reaction be carried out in the presence of an excess of a protic solvent, these processes are partly or entirely stopped, showing that the fluoride anion becomes engaged in H bonding to the protic solvent and no longer functions as a nucleophile.

One of the most striking features of the reactions described here is that these reactions should be rapid when the solubility of KF or indeed of any of the alkali metal fluorides in the protic solvents investigated is generally so low. Although the solubility of KF in molten phenol, benzoic acid, and 1,2-dihydroxybenzene is appreciable, the solubility of KF in the amines or in benzene thiol is less than 3 mol % at reflux temperatures. Indeed the solubility of KF in organic solvents, with the notable exceptions of carboxylic acids,[10] phenols, and some other hydroxylics, is generally very low. Maynard, in his studies on the fluorinating ability of KF in a variety of organic solvents,[3] found that even in the most efficient of the solvents he investigated (N-methylpyrrolidone), the solubility of KF was only about 3% at 190–200 °C. Although it is possible that these reactions could be occurring on the surface of suspended fluoride, it is more likely that the solubility of KF in these systems is enough to provide reaction—the solubilities of the inorganic products, potassium halide and potassium hydrogen bifluoride, in these protic solvents is probably lower than that of KF, which should encourage reaction to proceed (that KF is at all soluble in the protic solvents is probably a direct result of the H

bonding between solute and solvent). Parallel investigations on reactions involving tetraalkylammonium fluorides rather than metallic fluorides have shown that the former are generally more efficient in promoting condensation reactions of the type described here and as these fluorides are usually soluble in protic organic solvents it seems reasonable to assume that reactions occur in solution and not on the surface of undissolved fluoride.

The solubility of KF in DMF is around 3% at about 130 °C and DMF may indeed be used as a solvent for most of these reactions, its function being principally to solvate the potassium cation and having little influence on the fluoride anion other than to help carry it into solution. The reactions of KF–benzoic acid with halogenoalkanes suffered little in rate or yield on using DMF as solvent, whereas running the same reactions in the protic solvent methanol severely reduced the rates of reaction. The reason for the latter is probably twofold; primarily, methanol acts to lower the reaction temperature, and higher boiling alcohols were found to affect the rate less seriously.[49] However, there is a second reason and that is that methanol is a protic solvent and will compete with the acid for the fluoride anion. With carboxylic acids, the poorer electron acceptor methanol will have little influence on the very strong fluoride–acid H bond; however, with weaker electron acceptors such as the amines, it will seriously affect the H bond and indeed may alter the course of any reaction.[49] This clearly illustrates the importance of the choice of solvent in carrying out any reaction where H bonds may play a part in influencing the rate or course of that reaction.

The dramatic effect of the H bond on changing the rate or course of a reaction involving potential H bond electron acceptors and donors means that careful consideration must be given to any possible H bonding in a particular system before reaction should be attempted. In the cases of systems involving strong H bonding between fluoride and a hydroxyl-carrying organic compound, intramolecular or self-intermolecular condensations may occur. We have shown in other investigations on the role of H bonding in synthesis[50] that strong electron acceptors such as the enol forms of 1,3-cyclohexanedione and 2,4-pentanedione will undergo self-condensation in the presence of KF. Hence the possibility of competing homonuclear reactions should always be considered before attempting, for example, an heteronuclear condensation reaction.

Conclusion

We have shown in this account that beyond reasonable doubt, H bonding is capable of playing a significant role in organic synthesis. The selected systems covered here represent a range of H bond electron acceptors from the strong O–H to very weak S–H groups. It is clear, therefore, that the rate or even course of a reaction may be deliberately altered by introducing a strong electron donor such as fluoride capable of H bonding to an available electron acceptor site. It should also be clear that the significance of H bonding in synthesis may extend beyond deliberate attempts to introduce a strong electron acceptor or donor to a reaction system. It is difficult to think of any organic compound or simple inorganic salt that is truly incapable of forming H bonds. It was long thought, for example, that C–H groups were incapable of forming H bonds, yet now this field is so active that a considerable amount of the literature and even one book[51] have been devoted to this subject

alone. Where H bonding exists in a reaction system, the possibility of that bonding playing a definite role in determining the rate and perhaps the course of that reaction cannot be ruled out.

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