The first basicity scale of fluoro-, chloro-, bromo- and iodo-alkanes: some cross-comparisons with simple alkyl derivatives of other elements

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Formation constants (K_f) are determined for the 1 : 1 hydrogen-bonded complexes between 4-fluorophenol and 42 halogenoalkanes, in CCl_4 at 298 K, by FTIR spectrometry. A base parameter, $pK_{HB} = \log K_f$, has been defined which measures, for the first time, the relative hydrogen-bond acceptor strength of the halogens. Comparison with the basicity of group 15 and 16 elements shows that halogens are very weak bases, in the order: $N \gg O > P > S > Se > F > Cl \sim Br \sim I$. Attempts at correlations of pK_{HB} *vs.* electronegativity or *vs.* hardness lead to general scatter diagrams which may be partially resolved into separate trends within a given group of the periodic table. The pK_{HB} scale of halogenoalkanes extends from +0.26 for 1-fluoroadamantane to −0.70 for 1,1,1-trichloroethane (statistically corrected to −1.15 per chlorine atom). The main substituent effects explaining these pK_{HB} variations are for a given halogen: (*i*) field-inductive effects (polyhalogenoalkanes), (*ii*) resonance effects (cyclopropyl bromide), and (*iii*) polarizability effects (alkyl halides). The steric effects of bulky alkyl substituents do not appear to be significant since the basicity increases with the lengthening and branching of the alkyl groups (from methyl to 1-adamantyl). For a given halogen, pK_{HB} increases linearly with the infrared shift, $\Delta\nu(OH)$, produced by hydrogen bonding. However, as the group 17 is descended, IR shifts do not parallel pK_{HB}. An increasing sensitivity of IR shifts to polarizability is suggested when going from group 15 to group 17.

The basicity of organic molecules towards a special class of Lewis acids, the hydrogen-bond donors (*e.g.* alcohols), now called hydrogen-bond basicity,[1,2] is becoming increasingly important to measure. Indeed, the hydrogen bond is ubiquitous in chemistry[3] and biochemistry[4] and finds applications in fields as diverse as solid-state chemistry,[5] supramolecular chemistry,[6] chromatography,[7] pharmaceutical chemistry,[8] or stereochemistry.[9] The first systematic quantitative measurements of hydrogen-bond basicity go back to Arnett and Taft.[10,11] For technical reasons they chose 4-fluorophenol as the reference hydrogen-bond donor and measured the formation constants K_f of its hydrogen-bonded 1 : 1 complexes with organic bases B in CCl_4 at 298 K [eqns. (1) and (2)]. A logarithmic scale

$$B + 4\text{-}FC_6H_4OH \rightleftharpoons 4\text{-}FC_6H_4OH\cdots B \qquad (1)$$

$$K_f/\text{dm}^3\,\text{mol}^{-1} = [\text{HB complex}]/[B][4\text{-}FC_6H_4OH] \qquad (2)$$

$pK_{HB} = \log_{10} K_f$ was thus constructed and found to extend on *ca.* 3.5 pK units, *i.e.* 20 kJ mol^{-1} on the Gibbs energy scale, from thioethers to phosphine oxides.

Unfortunately, this scale was limited to a small number of bases, mainly oxygen and nitrogen bases.[10–12] Later on, we extended the pK_{HB} scale in order that chemists have at hand a scale approaching in importance the pK_a scale for Brønsted basicity. Through its linear transform[2] β_2^H, this pK_{HB} scale has already found wide application in linear solvation energy relationships,[13] in partition studies,[7] and for the prediction of the stability of many hydrogen-bonded complexes.[14] The pK_{HB} scale now extends over about 7 pK units and is presently available for alcohols, ethers, esters, amides, amidates, ketones, NO_2 and SO_2 bases, thioamides, π bases, amidines, pyridines and primary amines.[15]

These studies refer to carbon,[16] sulfur,[17] nitrogen[18] and oxygen[19] bases. Other atoms of the periodic table are however able to accept hydrogen bonds. Among them, halogen atoms seem the most interesting to study since they cover four periods and belong to the most electronegative group. The role of the electronegativity of atoms A and B in the hydrogen bond $A–H\cdots B$ has been emphasized by Pauling.[20] The quantitative comparison of the hydrogen-bond basicity of fluorine bases with oxygen and nitrogen bases, and of fluorine, chlorine, bromine and iodine bases between them, appears a necessary step for further theoretical work.

There exists a number of theoretical and structural studies[21] on the homodimers and heterodimers of hydrogen halides, but we almost completely lack experimental thermodynamic studies on the formation of intermolecular hydrogen bonds involving halogen atoms (we do not consider intramolecular hydrogen bonds in this work, since geometrical constraints might mask the intrinsic basicity of halogens). A literature survey on halogens bonded to sp^3 carbons (with sp^2 or sp carbons, the π site might compete with the halogen site) gives data which are (*i*) scarce, since only cyclohexyl,[22] n-heptyl,[23] isopropyl[24] and n-butyl halides[10] have been studied, (*ii*) inhomogeneous, because they refer to various hydrogen-bond donors: phenol,[22,23] 4-fluorophenol[10] or methanol,[24] and to various solvents, CCl_4,[22] C_2Cl_4[23] or pure base,[10] and (*iii*) contradictory. Low formation constants are always found, involving a small heat transfer in calorimetric studies[10] or low absorbance variations in spectroscopic works. Moreover, small IR OH shifts upon hydrogen bonding provoke the overlapping of the free and bonded OH bands and so prevent precise absorbance readings. These experimental difficulties explain why there was little incentive for chemists to study the basicity of halogens.

Today, the advantages of FTIR spectrometry give the chemist a tool of choice for measuring small quantities of complex, and curve-fitting software allows absorbance corrections to be made for overlapping bands. In this work we have determined, by means of FTIR spectrometry, the formation constants of

Table 1 Formation constant of the 4-fluorophenol–1-fluorooctane complex in CCl_4 at 25 °C (5 determinations)[a]

	0	1	2	3	4	5
C_a^O	4.800	4.862	4.783	4.893	4.888	4.842
C_b^O	0	71.39	140.92	280.30	419.22	556.97
Absorbance A	1.1315	1.074	0.973	0.886	0.792	0.724
$C_a = A/\varepsilon l$[b]		4.5562	4.1271	3.7577	3.3580	3.0729
$C_c = C_a^O - C_a$		0.3058	0.6561	1.1349	1.5303	1.7694
$C_b = C_b^O - C_c$		71.08	140.26	279.17	417.69	555.20
$K_f/\mathrm{dm^3\,mol^{-1}}$		0.94	1.13	1.08	1.09	1.04
Complex (%)[c]		6	14	23	31	37

[a] All concentrations in mmol dm^{-3}. C_a^O, C_b^O, C_a, C_b and C_c are respectively the initial and equilibrium concentrations of the donor (acid a), the acceptor (base b) and the complex c. [b] Beer–Lambert law: $\varepsilon = 1.1315/(4.8 \times 10^{-3}) = 235.7\ \mathrm{dm^3\,mol^{-1}\,cm^{-1}}$. [c] Complex (%) = $100 \times (C_c/C_a^O)$.

the hydrogen-bonded complexes of 4-fluorophenol with 42 halogenoalkanes in CCl_4 at 298 K. These data furnish a pK_{HB} scale of halogen bases which, to the best of our knowledge, is the first basicity scale of fluoro-, chloro-, bromo-, and iodo-alkanes. In order to assess the reliability of our values, we have compared pK_{HB} to $\Delta\nu(OH)$, the lowering of the $\nu(OH)$ frequency of 4-fluorophenol on going from the free to the hydrogen-bonded OH group generally being considered as a spectroscopic scale of hydrogen-bond basicity. The pK_{HB} scale also permits an approach to the important question of how hydrogen-bond basicity varies with position in the periodic table among compounds of such similar structures as amines, alcohols, sulfides, fluorides, chlorides, bromides and iodides. We have established structure–basicity relationships in the family of halogen bases for the first time. With this end in view, we have substituted the halogens with groups spanning a wide range of electronic and steric effects (with the constraint that most usual substituents which are more basic than the halogen function cannot be used in this analysis). Numerous alkyl substituents have been studied from methyl to pentyl (lengthening), *tert*-butyl (branching), cyclopropyl (resonance electron-withdrawing) and 1-adamantyl (high polarizability effect) and we have gradually increased the field electron-withdrawing effect of the halogenoalkyls, by decreasing the number of methylenes in the series $X(CH_2)_nX$. In doing so, we were able to obtain (approximate) formation constants down to dihalogenomethanes and even to 1,1,1-trichloroethane.

Experimental

Chemicals

Compounds were obtained from Aldrich, Lancaster and Fluorochem. They were carefully purified since they are all very weak bases and any trace of basic impurities will yield too high pK_{HB} values. This was for example the case of 1,3-difluoropropane, which was found to contain 2% acetone. We fractionally distilled this compound on a Podbielnak column and were able to obtain a GC purity of 99.8%.

1-Fluoroadamantane was prepared according to Fort and Schleyer[25] by reacting anhydrous 1-bromoadamantane with anhydrous silver fluoride in dry cyclohexane at reflux. Sublimation and recrystallization in petroleum ether gave a compound having mp 225 °C and an IR spectrum identical to literature.[26]

4-Fluorophenol was sublimed under vacuum and dried over P_2O_5. The spectroscopic grade CCl_4 was dried before use on activated molecular sieves (4 Å). All the procedures for the preparation of solutions and filling the IR cell were conducted in a dry glove box.

Spectra

IR spectra were recorded with a Bruker IFS48 Fourier transform spectrometer, at a resolution of 1 cm^{-1} with 256 scans. A 1 cm pathlength, infrared silica, constant temperature (25 ± 0.2 °C) cell was used.

Equilibrium constants

The equilibrium constant of eqn. (1) is defined by $K_f = C_c/C_aC_b$ where C_c, C_a and C_b are the equilibrium concentrations (mol dm^{-3}) of complex, acid (4-fluorophenol) and base (halogenoalkane) respectively. C_a is obtained from the IR absorbance of the free OH band at 3614 cm^{-1}. The infrared OH band of the complex occurs at a lower wavenumber but, nevertheless, generally contributes to the absorbance at the position of the free band. Accordingly, the spectra were treated with Curve Fit Bruker software, which enables overlapping bands to be mathematically resolved into their Gausso-Lorentzian components. K_f is calculated as illustrated in Table 1 for the example of 1-fluorooctane which gives $K_f = 1.06 \pm 0.09\ \mathrm{dm^3\,mol^{-1}}$ (95% confidence level).

Infrared wavenumbers shifts

The shifts of the OH vibration of 4-fluorophenol induced upon hydrogen bond formation are defined as: $\Delta\nu(OH) = 3614 - \nu(OH\cdots X)$. Because of the uncertainties introduced by the base concentration dependence[27] and the curve fit procedure, $\Delta\nu$ values are believed to be accurate to ±0.5–4 cm^{-1}.

Results

Table 2 summarizes the pK_{HB} scale constructed from the hydrogen bonding formation of 4-fluorophenol with 42 different halogenoalkanes in CCl_4 solution at 298 K. Also given are the corresponding values of $\Delta\nu(OH)$, the $\nu(OH)$ wavenumber shift between the free and hydrogen-bonded 4-fluorophenol.

Discussion

The place of halogenoalkanes and the effect of the atomic site of hydrogen bonding on the pK_{HB} scale

The pK_{HB} values of alkyl halides range from −0.06 to 0.26 for fluorides, −0.41 to −0.18 for chlorides, −0.40 to −0.17 for bromides and −0.47 to −0.19 for iodides. Clearly, these generally (39 out of 42) negative pK_{HB} values (*i.e.* $K_f < 1\ \mathrm{dm^3\,mol^{-1}}$) bear witness to the very weak hydrogen-bond basicity of halogenoalkanes. The less weakly basic ones are fluorides, while chlorides, bromides and iodides have the same weakness, within experimental uncertainty. Other weak hydrogen-bond bases are π bases[16] and the following basicity order is observed for halogen and π bases.

PentF > BuC≡CH > PentBr ~ PentI ~ PentCl > C_6H_6 >
−0.06 −0.22 −0.35 −0.37 −0.38 −0.49
PentCH=CH_2
−0.67

The pK_{HB} values obtained in this work for atoms belonging to four periods of the periodic table allow us to study the effect of the atomic site of hydrogen bonding on the hydrogen bond acceptor strength. The question of how basicity varies with

Table 2 Hydrogen-bond basicity of halogenoalkanes: the thermodynamic pK_{HB} scale and the spectroscopic $\Delta\nu$(OH) scale

No.	Compound	pK_{HB}	$\Delta\nu$(OH)/cm^{-1}
Fluoroalkanes			
1	1,3-Difluoropropane	0.03 (−0.27)[a]	31.6
2	1-Fluoropentane	−0.06	44
3	1-Fluorooctane	0.02	43.8
4	Fluorocyclohexane	0.09	58.7
5	1-Fluoroadamantane	0.26	69.9
Chloroalkanes			
6	1,1,1-Trichloroethane	−0.70 (−1.15)[b]	13
7	Dichloromethane	−0.50 (−0.80)[a]	18.2
8	1,1-Dichloroethane	−0.42 (−0.72)[a]	22
9	1,2-Dichloroethane	−0.31 (−0.61)[a]	37
10	1,3-Dichloropropane	−0.21 (−0.51)[a]	48
11	1,4-Dichlorobutane	−0.17 (−0.47)[a]	57.5
12	1-Chlorobutane	−0.41	64.7
13	1,5-Dichloropentane	−0.09 (−0.39)[a]	58.5
14	1-Chloropentane	−0.38	63
15	2-Chloropropane	−0.30	72
16	Chlorocyclohexane	−0.27	76.9
17	2-Chloro-2-methylpropane	−0.28	80
18	1-Chloroadamantane	−0.18	86.5
Bromoalkanes			
19	Dibromomethane	−0.40 (−0.70)[a]	26.3
20	1,2-Dibromoethane	−0.33 (−0.63)[a]	45.9
21	1,3-Dibromopropane	−0.23 (−0.53)[a]	60.1
22	Bromocyclopropane	−0.47	62.4
23	1,4-Dibromobutane	−0.17 (−0.47)[a]	69.8
24	Bromoethane	−0.40	73.5
25	1-Bromopropane	−0.38	75.4
26	1-Bromopentane	−0.35	75.8
27	1-Bromobutane	−0.34	75.7
28	2-Bromopropane	−0.30	83.8
29	Bromocyclohexane	−0.25	88
30	2-Bromo-2-methylpropane	−0.22	91.4
31	1-Bromoadamantane	−0.17	97
Iodoalkanes			
32	Diiodomethane	−0.38 (−0.68)[a]	40
33	1,2-Diiodoethane	−0.35 (−0.65)[a]	53
34	1,3-Diiodopropane	−0.21 (−0.51)[a]	66
35	Iodomethane	−0.47	68.2
36	Iodoethane	−0.47	76
37	1,4-Diiodobutane	−0.16 (−0.46)[a]	74.3
38	1-Iodopentane	−0.37	79
39	2-Iodopropane	−0.37	85
40	2-Iodo-2-methylpropane	−0.33	95.4
41	Iodocyclohexane	−0.32	91.5
42	1-Iodoadamantane	−0.19	101

[a] The K_f value is divided by 2 to put this pK_{HB} value on a per halogen basis. [b] The K_f value is divided by 3.

Table 3 Comparable bases: pK_{HB} and $\Delta\nu$(OH) values and absolute electronegativity χ[a] and hardness η[a] of their heteroatomic hydrogen bonding site

Base	pK_{HB}	χ/eV	η/eV	$\Delta\nu$(OH)/cm^{-1}[g]
$EtNH_2$	2.17[b]	7.27	7.27	351
Et_3P	~0.84[c]	5.62	4.86	264
Et_2O	1.01[d]	7.53	6.08	150
Et_2S	0.22[e]	6.22	4.12	146
Et_2Se	0.14[e]	5.89	3.86	145
PentF	−0.06[f]	10.41	7.01	10
PentCl	−0.38[f]	8.31	4.70	26
PentBr	−0.35[f]	7.60	4.24	35
PentI	−0.37[f]	6.76	3.70	41

[a] $\chi = (I + A)/2$, $\eta = (I - A)/2$ (I is the ionization energy and A the electron affinity) (ref. 29). [b] Ref. 33. [c] Calculated from the generalized equation for the formation of hydrogen-bonded complexes (ref. 14) applied to the $PhCH_2OH–Et_3P$ complex in benzene: $\log K_f = -1.035 + 6.328\alpha\beta$; α and β are hydrogen-bond acidity and basicity parameters, respectively. $\alpha(PhCH_2OH) = 0.3915$ (ref. 39); $\log K_f = 0$ (ref. 40); thus $\beta(Et_3P) = 0.418$ and $pK_{HB} = 4.636\beta - 1.1$ (ref. 2). [d] Ref. 15. [e] Ref. 2. [f] This work. [g] This work; $\Delta\nu(OH) = \nu(\text{free MeOH}) - \nu(MeOH\cdots X)$. Methanol is used because the 4-fluorophenol shift cannot be measured for $EtNH_2$.

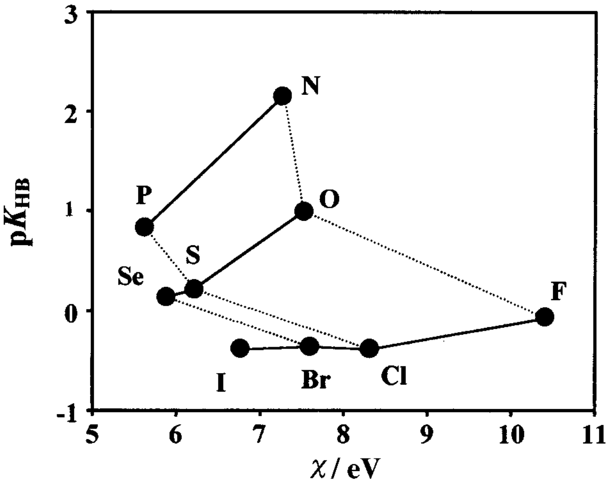

Fig. 1 Plot of the hydrogen-bond basicity *vs.* the electronegativity of the hydrogen-bond acceptor atom (data from Table 3).

position in the periodic table among compounds of such similar structures as amines, phosphines, ethers, sulfides, selenides or halides, is a matter of fundamental importance since basicity is about the only chemical property that all these compounds have in common. Since pK_{HB} values of most hydrides have not yet been determined and the fact that alkyl substituents introduce large effects, we have tabulated pK_{HB} values for organic functionalities with comparable alkyl substituents, when possible (Table 3). We have also given in this table two fundamental properties of the heteroatom, the absolute electronegativity[28] and its companion parameter, the absolute hardness.[29] The role of electronegativity on the hydrogen bond strength has been emphasized by many authors.[20] Moreover, since hydrogen bond donors are hard acids in the hard and soft classification of acids and bases,[30] we expect that 4-fluorophenol will like hard bases, according to the HSAB principle.[30]

Contrary to Pauling's statement[20] that "the strength of the [hydrogen] bond should increase with increase in the electronegativity of the two bonded atoms" (X and Y in X–H···Y), we do not find any correlation between pK_{HB} and electronegativity (correlation coefficient $r = 0.21$ for $n = 9$ points). We even find that in a given period there is a sharp and steady decrease in pK_{HB} with increasing electronegativity, regardless of the row under consideration (Fig. 1, dashed lines). Regarding pK_{HB}, Pauling's statement is only obeyed within a given group (Fig. 1, full lines). This gives the basicity orders N ⩾ P and O ⩾ S > Se and F > Cl ~ Br ~ I.

The poor correlation ($r = 0.65$, $n = 9$) between pK_{HB} and hardness is illustrated in Fig. 2. The HSAB principle appears to be obeyed only within a given group (full lines). However by restricting the HASB principle to bases of a given electronegativity ("Among potential partners of a given electronegativity, hard likes hard and soft likes soft"),[31] *e.g.* Br, O and N which have $\chi = 7.60$, 7.53 and 7.27 respectively, the dashed line illustrates the almost linear increase of pK_{HB} with hardness.

These preliminary observations need to be accommodated in the theory of the hydrogen bond. χ and η will probably have to be replaced by descriptors of the electrostatic, induction, dispersion, charge transfer and exchange repulsion forces contributing to the hydrogen bond energy. Nevertheless these

Table 4 Analysis of pK_{HB} by $pK_{HB} = \rho_\alpha \sigma_\alpha + i$[a]

RX	ρ_α[b]	i[c]	n[d]	r[e]	s[f]	F[g]
RF	−0.760	−0.470	4	0.972	0.04	34
RCl	−0.535	−0.681	6	0.944	0.03	32
RBr	−0.520	−0.643	8	0.972	0.02	104
RI	−0.472	−0.663	7	0.964	0.03	67

[a] The σ_α values are from ref. 38 or calculated from eqn. (5). [b] The regression coefficient (sensitivity to polarizability effects) is negative because alkyl halides are made more basic by more polarizable alkyl substituents (with larger $-\sigma_\alpha$ value). [c] The intercept i gives a rough estimation of pK_{HB} for the hydrides HX ($\sigma_\alpha = 0$ for hydrogen). [d] Number of alkyl substituents. [e] Correlation coefficient. [f] Standard deviation. [g] Fisher test.

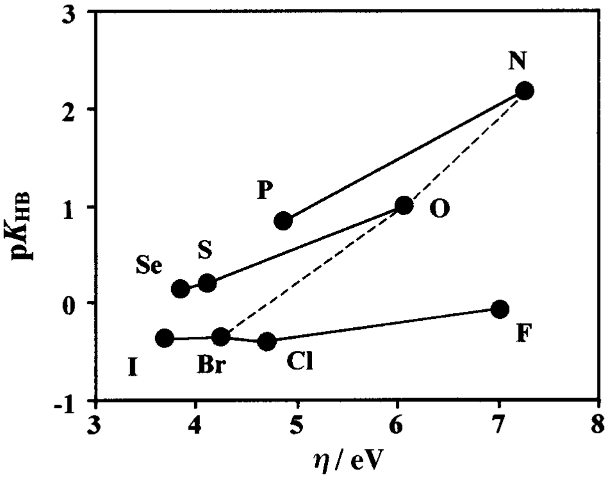

Fig. 2 Plot of the hydrogen-bond basicity *vs.* the hardness of the hydrogen-bond acceptor atom (data from Table 3).

observations are possibly useful for the classification of atomic centres of hydrogen bonding and the prediction of the behaviour of arsines, stilbines and tellurides.

Structure–hydrogen-bond basicity relationships

Alkyl fluorides **2**–**5**, alkyl chlorides **12**, **14**–**18**, alkyl bromides **24**–**31** and alkyl iodides **35**, **36**, **38**–**42** generally show an increase of hydrogen-bond basicity both on chain lengthening in the order: Et < Pr < Bu < Pent < Oct and on chain branching in the order: Et < *i*Pr < *t*Bu and c-Hex < 1-Adam. Since alkyl substituents are found to operate in the reverse order of steric hindrance, steric effects do not predominate in the pK_{HB} variation of alkyl halides, and we attribute the alkyl effect mainly to an electronic effect. In this respect alkyl halides behave like alcohols[32] and primary amines,[33] but differently from ethers[15] and amidines.[34] For the gas-phase protonation of alkyl-substituted bases the increase of basicity on chain lengthening and branching was interpreted[35] as being the result of induced dipole stabilization by the alkyl substituent of the ion formed on protonation. It has been correlated with the polarizability substituent constant[36] σ_α, calculated from the substituent polarization potentials of CH_3X compounds which result from polarization of the X substituents by a full positive charge placed 3 Å from the carbon atom. The pK_{HB} of alkyl halides appears well correlated with σ_α (Table 4).

With a pK_{HB} of −0.47 cyclopropyl bromide does not obey the polarizability equation, and appears a weaker base than the related non-cyclic *i*PrBr ($pK_{HB} = -0.30$). This lower basicity can be interpreted in terms of an electron-withdrawing resonance effect of the cyclopropyl substituent. The shorter C–Br bond length in cyclopropyl bromide compared to methyl bromide (0.04 Å)[37] is also evidence of an appreciable resonance interaction of the bromide lone-pair electrons with the ring.

Table 5 Analysis of pK_{HB} by $pK_{HB} = \rho_\alpha \sigma_\alpha + \rho_F \sigma_F + i$[a]

RX	ρ_α	ρ_F	i	r	n	s	F
RCl	−0.576	−1.771	−0.718	0.988	11	0.03	163
RBr	−0.559	−1.742	−0.689	0.950	12	0.06	41

[a] The σ_α and σ_F values are from ref. 38 or calculated through eqns. (4) and (5).

We have studied a number of dihalogenoalkanes $X^1(CH_2)_nX^2$ in order to quantify the electron-withdrawing field effect of the C–X¹ dipole on the X² lone-pairs basicity (and *vice versa*). The comparison with monohalogenoalkane is made on a per halogen atom basis by subtracting log 2 from pK_{HB}, assuming the same basicity for each halogen. As expected from the field effect distance dependence, the basicity decreases when decreasing the number of methylene groups. No quantitative study of the field effect appears feasible without first determining the structures and the populations of the numerous rotamers of dihalogenoalkanes. However we have found a satisfactory relationship between pK_{HB} and the field substituent constant σ_F through eqn. (3), by assuming a constant fall-off factor for transmission

$$pK_{HB} = \rho_\alpha \sigma_\alpha + \rho_F \sigma_F + i \qquad (3)$$

of dipolar effects in a homologous straight chain [eqn. (4)]. We

$$\sigma_F(XCH_2) = \sigma_F(X)/1.95 \qquad (4)$$

have adopted for hydrogen-bond acid–base equilibria in an apolar solvent, the attenuation factor of 1/1.95 per methylene found valid for Brønsted acid–base equilibria in the gas phase.[35] We have also adopted eqn. (5),[35] from the same

$$\sigma_\alpha(XCH_2) = \sigma_\alpha(CH_3) + [\sigma_\alpha(X)/2.3] \qquad (5)$$

equilibria, for the calculation of untabulated σ_α values. The analysis of pK_{HB} by eqn. (3) is reported in Table 5 for chloroalkanes and bromoalkanes only, since $F(CH_2)_n$ substituents are lacking in our sample and σ_α is not tabulated for iodine in ref. 38. The equations of Tables 4 and 5 seem rather robust since the addition of a $\rho_F\ \sigma_F$ term does not much change the ρ_α and i values. The ratio ρ_F/ρ_α is the same for the two series at *ca.* 3, showing that the field effect is the most important mechanism of substituent effect in chloroalkanes and bromoalkanes. The high sensitivity to the field effect explains why CH_2Cl_2, CH_2Br_2 and CH_3CCl_3 are so weakly basic. However this basicity remains measurable (a new OH · · · X band is observed in the IR spectra of their complexes with $4\text{-}FC_6H_4OH$). When these compounds are used as solvents, these results show that the halogens ability to accept hydrogen bonds constitute one of their solvation mechanisms.

Relationship between pK_{HB} and the shift of the OH stretching frequency

The Δν(OH) shift which the OH stretching frequency undergoes when the hydrogen bond is formed [eqn. (1)], has often been correlated to the energetics of hydrogen bonding.[3,21] It is well established for O, N, S and π bases that Δν(OH) increases with the Gibbs energy of hydrogen bond formation (*i.e.* pK_{HB}), according to family-dependent linear relationships.[15–19] In this context a family is defined as a series of bases that possess the same hydrogen-bond acceptor atom in the same hybridization state. For example nitriles (N sp), pyridines (N sp²), ketones (O sp²) and ethers (O sp³) trace different lines in the ΔG–Δν plane. For the reason that ΔG is more sensitive to steric effects, through its entropic term, than Δν, the main condition for a good family-dependent ΔG–Δν relationship to be observed is that the steric effects on the hydrogen-bond acceptor site remain almost constant. Thus, 2-alkyl- and 2,6-

Table 6 Statistics of the regression $pK_{HB} = a\Delta\nu(OH) + i$

RX	*a*	*i*	*n*	*r*	*s*	*F*
RF	0.0129	−0.64	5	0.982	0.04	83
RCl	0.0104	−1.06	13	0.950	0.09	102
RBr	0.0080	−0.97	13	0.980	0.03	262
RI	0.0077	−1.02	11	0.973	0.04	161

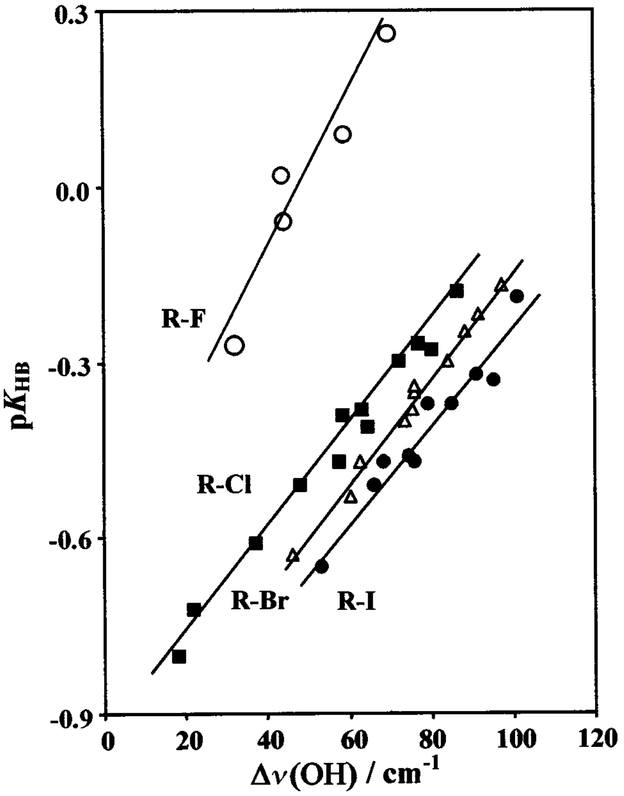

Fig. 3 Hydrogen-bond basicity pK_{HB} of fluoroalkanes (○), chloroalkanes (■), bromoalkanes (△) and iodoalkanes (●) *vs.* IR shifts of 4-fluorophenyl (data from Table 2). For the sake of clarity, points 6, 19, 23 and 32 are excluded.

dialkyl-substituted pyridines stand below the line traced through the 3- and 4-substituted pyridines,[18] and deviations increase with the alkyl size, because of steric hindrance of the nitrogen lone pair.

Halogenoalkanes trace four different lines in the pK_{HB}–$\Delta\nu$(OH) plane (Fig. 3). The correlations reported in Table 6 are good. An analysis of residuals does not show any significant negative deviations of the bulky substituents. From these observations we draw the following conclusions. Firstly, the ΔG–$\Delta\nu$ relationship depends on the nature of the hydrogen-bond acceptor atom, even for closely related atoms of the same basicity, such as Cl, Br and I. Secondly, the quality of the correlations supports our expectation that the photometric accuracy of FTIR spectrometry and the curve-fitting procedures, in addition to careful purification, allow us to measure with satisfactory precision even very low hydrogen-bond formation constants. Lastly, steric effects do not decrease significantly the hydrogen-bond basicity of halogenoalkanes, as already seen from the positive correlation of alkyl effects with σ_α.

Surprisingly, the sequence of IR shifts, RF ⩽ RCl < RBr < RI, lies in the reverse order of pK_{HB} values, RI ~ RBr ~ RCl < RF. This matter may be thrown into some perspective by comparison of analogous bases of group 15, 16 and 17 elements (Table 3 and Fig. 4). Within a given period the thermodynamic and spectral basicity orders remain the same (F < O < N and Cl < S < P and Br < Se; dashed lines of Fig. 4).

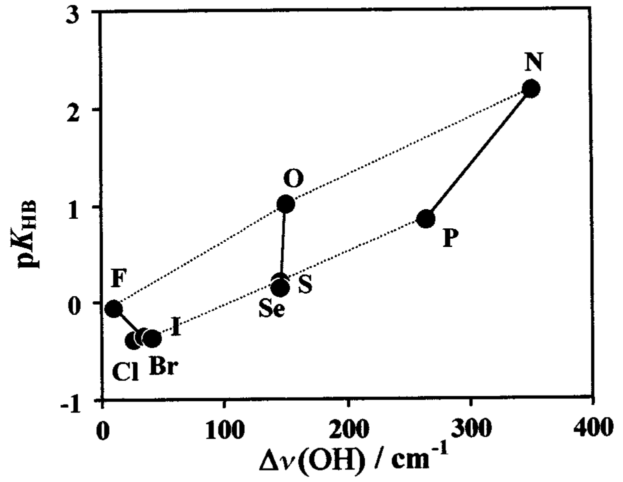

Fig. 4 Plot of the hydrogen-bond basicity pK_{HB} *vs.* the IR shift of methanol (data from Table 3).

Within a given group (full lines of Fig. 4), the slope of the pK_{HB}–$\Delta\nu$ relationship appears to change regularly from group 15 to group 17, being positive for group 15, almost zero for group 16, and negative for group 17. Theoretical calculations on hydrogen bonding systems with heavy atoms are not sufficiently developed at present to explain these observations. We can only remark that a factor related to polarizability (or volume, van der Waals radius or distance H···X) gains importance in IR shifts relative to ΔG in going from group 15 to group 17.

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