The Hydrogen-Bond Basicity pK_{HB} Scale of Peroxides and Ethers

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Using 4-fluorophenol as a reference hydrogen-bond donor, equilibrium constants, K_f, for the formation of 1:1 hydrogen-bonded complexes have been obtained by FTIR spectrometry for 39 ethers of widely different structure (cyclic and acyclic ethers, crown ethers, glymes, acetals, orthoesters, and disiloxane) and 3 peroxides, in CCl_4 at 298 K. The pK_{HB} scale of monoethers extends from 1.44 for 2,3-diadamant-2-yloxirane to –0.53 for hexamethyldisiloxane. The main effects explaining the variation of the hydrogen-bond basicity of sp^3 oxygen atoms are (i) the electron-withdrawing field-inductive effect [e.g. in $(CF_3)_2CHOMe$], (ii) the electron-withdrawing resonance effect (e.g. in $EtOCH{=}CH_2$) (iii) the steric effect (e.g. in tBu_2O), (iv) the lone-pair–lone-pair repulsion (e.g. in cyclic peroxides), and (v) the cyclization giving the basicity order: oxetane > tetrahydrofuran > tetrahydropyran > oxirane. A spectroscopic scale of hydrogen-bond basicity is constructed from the infrared frequency shift Δν(OH) of methanol hydrogen-bonded to peroxides and ethers. The thermodynamic pK_{HB} scale does not correlate with the Δν(OH) scale because of (i) statistical effects in polyethers and peroxides (ii) secondary hydrogen-bond acceptor sites (e.g. in benzyl ether), (iii) variations of the s character of oxygen lone pairs either by conjugation or cyclization, (iv) steric effects, (v) lone-pair–lone-pair repulsions, and (vi) anomeric effects. The ν(OH···O) band shape reveals two stereoisomeric complexes, the most stable being tetrahedral at the ether oxygen atom.

Since the work of Taft et al.[1] and Arnett et al.[2], 4-fluorophenol has proved to be an excellent reference hydrogen-bond donor for the establishment of a thermodynamic hydrogen-bond basicity scale for organic bases B. This scale, denoted by pK_{HB}, is defined as the logarithm of the formation constant K_f of the 1:1 hydrogen-bonded complex $4\text{-}FC_6H_4OH\cdots B$ in CCl_4 at 298 K [eqs. 1−3].

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

$$K_f / l\ mol^{-1} = [complex] / [4\text{-}FC_6H_4OH]\cdot[Base] \quad (2)$$

$$pK_{HB} = \log_{10}K_f \quad (3)$$

The choice of these standard conditions allows the accurate determination of K_f in a wide basicity range by various techniques (^{19}F NMR[1], UV[2], calorimetry[3]) giving almost identical results[4]. Linear free-energy relationships indicate[5] that the lowest limit of the pK_{HB} scale measurable in CCl_4 at 298 K is ca. −1.1. For neutral bases we have indications[6] that the pK_{HB} scale can be extended to ca. 6. Thus, this basicity scale extends, at least, on a 7 pK units range and a 40 kJ mol^{-1} Gibbs energy range.

The building of the pK_{HB} scale contributes not only to the increasing efforts towards a quantitative description of the hydrogen bond, but also to the difficult and unachieved task of measuring quantitatively the strength of organic Lewis bases. We have already measured pK_{HB} for nitrogen[7], oxygen, sulfur[8], and π[9] bases. In the case of oxygen bases, alcohols[10], esters[11], amides[12], ketones[13], nitro bases[14], sulfonyl bases[15], and amidates[16] have already been studied. We present here the pK_{HB} scale for peroxides and (mainly) ethers.

To our knowledge, no formation constant for the hydrogen-bonded complex between any hydrogen-bond donor and any peroxide seems available. In the case of ethers, numerous measurements of hydrogen-bond formation constants have been reported[17][18][19][20][21][22][23][24]. However they generally refer to a too limited number of compounds for giving a wide view on the influence of structure on ether hydrogen-bond basicity. Moreover, they were carried out with different hydrogen-bond donors (methanol[19], phenols[17][18][20][22][23][24], isothiocyanic acid[21]), different solvents (cyclohexane[24] and carbon tetrachloride) and different temperatures. Statistical procedures should be used to set up an homogeneous basicity scale from these data and this would inevitably result in a loss of fine structural informations. We prefer building a scale defined from a reference process (eq. 1) rather than a statistical scale.

We have used FTIR spectrometry in this work since this technique brings many additional informations on hydrogen-bonded complexes.

The equilibrium concentrations of the different species in eq. (1) can be obtained from the absorbances of the O−H stretching of 4-fluorophenol at 3614 cm^{-1} for different initial base concentrations. Therefore, we have first determined the pK_{HB} values of 3 peroxides and 39 ethers including crown ethers, glymes, acetals, orthoesters, and one disiloxane. The case of aromatic ethers, which are not only

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oxygen bases but also π bases, will be studied in a future paper. We have found that the ether pK_{HB} scale extends on ca. 2.5 pK units and the main effects governing these variations is discussed.

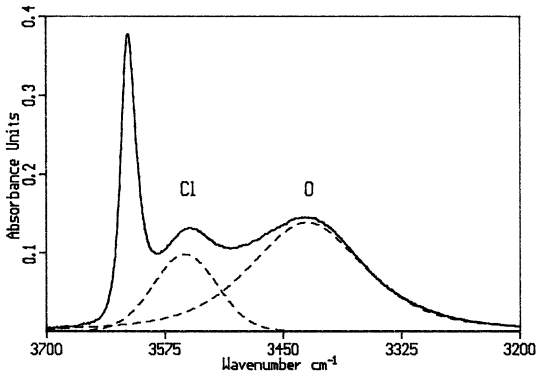
Secondly, we have measured the methanol and 4-fluorophenol O−H stretching wavenumber shifts between the free and the hydrogen-bonded OH group. These shifts are often considered as spectroscopic scales of hydrogen-bond basicity and their comparison with the thermodynamic pK_{HB} scale reveals steric and anomeric effects and variations in the hybridization state of the oxygen lone pairs.

At last, IR spectrometry has revealed, from the ν(OH···O) band shape and through deconvolution procedures, the existence of two stereoisomers for many hydrogen-bonded ethers. This stereoisomerism of the hydrogen-bond formation, already known for ketones[25][26][27], does not seem to have been previously described for ethers.

Results

The pK_{HB} values are compiled in Table 1. For a few X-substituted ethers bearing a second hydrogen-bond acceptor site X, the presence in the IR spectra of a second ν(OH···X) band, in addition to the ν(OH···O) band (Figure 1), shows that two 1:1 hydrogen-bonded complexes are formed in solution, the OH···O and the OH···X complexes.

Figure 1. IR spectrum of the association of 4-fluorophenol (0.004 M) with bis(2-chloroethyl)ether (0.6 M) in CCl_4; two 1:1 complexes are observed and attributed to adducts to the chlorine atom (Cl) and to the oxygen atom (O)



It is easy to demonstrate that the measured formation constant K_f (with ether in excess in order to avoid the formation of 2:1 complexes) is a global constant corresponding to the sum of the formation constants of two 1:1 complexes:

$$K_f = K_f(X) + K_f(O) \quad (4)$$

In the same way, eq. (5) applies to polyethers and peroxides. In this case,

$$K_f = \sum_{i=1}^{n} K_f(O_i) \quad (5)$$

if the oxygen atoms are equivalent or if we assume that they have almost the same basicity, it is easy to refer to the basicity of one oxygen atom by applying the statistical correction $-\log n$ to pK_{HB}. The results are shown in parentheses in Table 1.

According to eq. (4), we have to substract $K_f(X)$ in order to obtain the true ether basicity $K_f(O)$. We have evaluated $K_f(X)$ by using relationships between p$K_{HB}(X)$ and $\Delta\nu$(OH···X) established in the families of π bases[9] and of chloroalkanes[31]. The results are presented in Table 2, and p$K_{HB}(O)$ are reported in parentheses in Table 1 for dibenzyl ether (**10**), 2-chloroethyl ethyl ether (**13**) and bis(2-chloroethyl) ether (**16**). The pK_{HB} values remain uncorrected for the compounds **9**, **15**, **17**, **20**, **32**, **35**, **37**, and **38** because it does not appear any detectable ν(OH···π), ν(OH···Cl), or ν(OH···F) bands in the IR spectra of their complexes with 4-fluorophenol.

Literature measurements[17][18][19][20][21][22][23][24] of the formation constants K for 1:1 hydrogen-bonded complexes between ethers and various hydrogen-bond donors have been compared to our pK_{HB} scale via the linear free-energy relationship (6)

$$pK_{HB} = \alpha \log K + \beta \quad (6)$$

and the results are presented in Table 3. Our pK_{HB} scale agrees (mean correlation coefficient $r_m = 0.983$) with the literature, and the agreement is excellent ($r_m = 0.995$) when very few important outliers are excluded. The fact that these excluded data disagree only in one data set (i.e. agree with pK_{HB} in all other sets) indicates a greater reliability of our results.

The wavenumber shifts $\Delta\nu_1$(OH) of methanol and $\Delta\nu_2$(OH) of 4-fluorophenol are also reported in Table 1. For methanol the ν_1(OH···O) band is roughly symmetrical if we exclude the peroxides and epoxides. For 4-fluorophenol the ν_2(OH···O) band appears in many cases as flat and abnormally broad or presents a shoulder. These shapes signify the presence of two overlapping bands. The existence of two bands is particulary evident in epoxides and peroxides, and they are even resolved in diadamantyloxirane **21**. We have mathematically resolved these broad bands into two Gauss-Lorentz-type components, as illustrated in Figure 2, and the wavenumber shifts corresponding to the component maxima are reported in Table 1.

Figure 2. IR spectrum of the association of 4-fluorophenol (0.004 M) with 2,3-diadamant-2-yloxirane (0.02 M) in CCl_4; the two 1:1 complexes are attributed to structures **A** and **B** shown in Figure 3

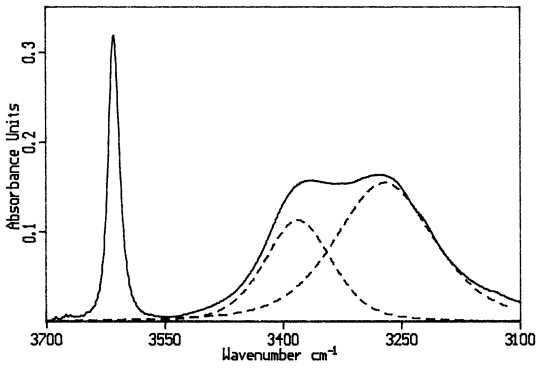
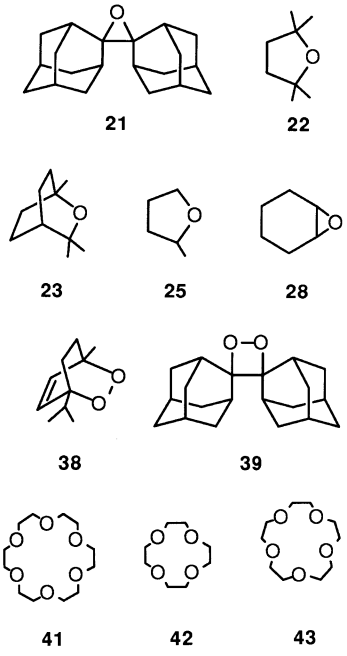


Table 1. Hydrogen-bond basicity of ethers and peroxydes: IR shifts of methanol [$\Delta\nu_1$(OH)/cm^{-1}] and 4-fluorophenol [$\Delta\nu_2$(OH)/cm^{-1}] and pK_{HB} values

No	Compound	Formula	$\Delta\nu_1$(OH)	$\Delta\nu_2$(OH)	pK_{HB}
	Acylic ethers				
1	*Tert*-butyl methyl ether	*t*BuOMe	166	315, 186	1.19
2	Diisopropyl ether	iPr_2O	164	310, 188	1.11
3	1,2-Diethoxyethane	$EtOCH_2CH_2OEt$	133	265	1.39 (1.09)[a]
4	*Tert*-butyl ethyl ether	*t*BuOEt	165	318, 183	1.08
5	1,2-Dimethoxyethane	$MeOCH_2CH_2OMe$	125	249	1.32 (1.02)[a]
6	Diethyl ether	Et_2O	150	290	1.01
7	Dibutyl ether	nBu_2O	154	293, 174	0.88
8	Di-*tert*-butyl ether	tBu_2O	168	328, 218	0.75
9	Diallyl ether	$(H_2C{=}CHCH_2)_2O$	127	252	0.70
10	Dibenzyl ether	$(PhCH_2)_2O$	129	249, 52π	0.72 (0.65)[b]
11	Dimethoxymethane	$(MeO)_2CH_2$	117	235	0.88 (0.58)[a]
12	Trimethyl orthoformate	$(MeO)_3CH$	89	187	1.02 (0.55)[a]
13	2-Chloroethyl ethyl ether	$EtOCH_2CH_2Cl$	117	237, 87^{Cl}	0.55 (0.44)[b]
14	Tetramethyl orthocarbonate	$(MeO)_4C$	82	181	0.86 (0.26)[a]
15	Ethyl vinyl ether	$EtOCH{=}CH_2$	70	165	0.10
16	Bis(2-Chloroethyl) ether	$(ClCH_2CH_2)_2O$	78	190, 67^{Cl}	0.27 (-0.03)[b]
17	Dichloromethyl methyl ether	$MeOCHCl_2$	-	114, 17^{Cl}	-0.09
18	Hexamethyldisiloxane	$(Me_3Si)_2O$	79	186	-0.53
19	Ethyl ethynyl ether	$EtOC{\equiv}CH$	~ 50	126	
20	1,1,1,3,3,3-Hexafluoro-isopropyl methyl ether	$MeOCH(CF_3)_2$	-	65	~ -0,41
	Cyclic ethers				
21	2,3-diadamant-2-yl oxirane	[c]	129,180	338, 234	1.44
22	2,2,5,5-Tetramethyltetrahydro-furan	[c]	185	339, 214	1.43
23	Cineole (eucalyptol)	[c]	185	347, 230	1.38
24	Trimethylene oxide (oxetane)	$\overline{CH_2(CH_2)_2O}$	157	295	1.36
25	2-Methyltetrahydrofuran	[c]	160	306	1.34
26	Tetrahydrofuran	$\overline{CH_2(CH_2)_3O}$	158	301	1.28
27	Tetrahydropyran	$\overline{CH_2(CH_2)_4O}$	157	299, 165	1.23
28	Cyclohexene oxide	[c]	118	258, 181	1.13
29	Propylene oxide	$Me\overline{CHCH_2O}$	104	258, 167	0.97
30	1,4-Dioxane	$\overline{CH_2CH_2OCH_2CH_2O}$	126	248	1.03 (0.73)[a]
31	1,3-Dioxane	$\overline{CH_2CH_2CH_2OCH_2O}$	107	220	0.93 (0.63)[a]
32	2,3-Dihydrofuran	$\overline{CH{=}CHCH_2CH_2O}$	86	187	0.53
33	1,3-Dioxolane	$\overline{CH_2CH_2OCH_2O}$	94	192	0.75 (0.45)[a]
34	Epichlorhydrin	$ClCH_2\overline{CHCH_2O}$	72	202, 122	0.44
35	3,4-Dihydro-2*H*-pyran	$\overline{CH{=}CH(CH_2)_3O}$	83	192	0.41
36	1,3,5-Trioxane	$\overline{CH_2OCH_2OCH_2O}$	60	157	0.50 (0.02)[a]
37	Furan	$\overline{CH{=}CH\text{-}O\text{-}CH{=}CH}$	~16	55	-0.40
	Peroxides				
38	Ascaridole	[c]	80	210, 139	1.22 (0.92)[a]
39	3,4-diadamant-2-yl dioxetan	[c]	68	232, 148	0.93 (0.63)[a]
40	*Tert*-butyl peroxide	*t*BuO-O*t*Bu	101	145, 230	0.43 (0.13)[a]
	Crown ethers				
41	18-Crown-6	[c]	134	264	1.98 (1.20)[a]
42	12-Crown-4	[c]	143	270	1.73 (1.13)[a]
43	15-Crown-5	[c]	141	276	1.82 (1.12)[a]



[a] Statistically corrected. – [b] Value corrected for the presence of a second accepting group. – [c] See formulae.

Discussion

The Two 1:1 Complexes of 4-Fluorophenol with Ethers

We have attributed the two OH stretching bands of the 4-FC_6H_4OH–ether complexes to complexes of different geometries on the following grounds. Firstly the OD stretching bands of the 4-fluorophenol[D] complexes keep the same shape that of the OH ones: this makes improbable the attribution of the doublet to a Fermi resonance. Secondly, temperature effects (from −6 to +55°C in CCl_4) show that the two band intensities decrease reversibly at the benefit of the free band at 3614 cm^{-1} as the temperature of

Table 2. Evaluation of the oxygen hydrogen-bond basicity $K_f(O)$ when a second basic center X is present in the molecule

No.	Compound	K_f[a][b]	$\Delta\nu$(OH···X)[c]	$K_f(X)$[a]	$K_f(O)$[a][d]
10	dibenzyl ether	5.25	55.6	0.39[e]	4.48
13	2-chloroethyl ethyl ether	3.55	87	0.78[f]	2.78
16	bis(2-chloroethyl) ether	1.85	67	0.46[f]	0.94

[a] 1 mol^{-1}. – [b] $K_f = 10\ pK_{HB}$. – [c] cm^{-1}. – [d] $K_f(O) = K_f - n\,K_f(X)$. – [e] Calculated[9] from $pK_{HB}(\pi) = 0.0109\ \Delta\nu(OH\cdots\pi) - 1.02$. – [f] Calculated[31] from $pK_{HB}(Cl) = 0.0115\ \Delta\nu(OH\cdots Cl) - 1.11$.

lowing sequences in the percentage of **B** from infrared intensities:

2,2,5,5-tetramethyltetrahydrofuran > tetrahydrofuran
$tBu_2O > iPr_2O > Et_2O$
$tBu_2O > t$BuOEt > tBuOMe

Moreover, the crystallographic scatterplots illustrating the position of hydrogen-donor atoms involved in hydrogen bonding to sp^3 oxygen atoms show[38] a cluster corresponding to geometry **B** more marked for epoxides than for other

Table 3. Results of the correlations $pK_{HB} = \alpha \log K + \beta$ between the equilibrium constants for the association of ethers with 4-fluorophenol (pK_{HB}) and other hydrogen-bond donors (log K)

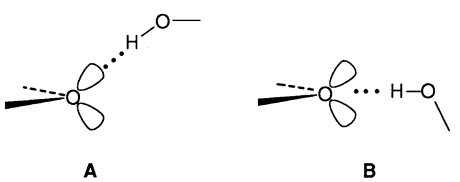
Set no.	Hydrogen-bond donor, temperature, solvent	α	β	N[a]	r[b]	s[c]	Ref.
1	Phenol, 293 K, CCl_4	0.967	−0.062	11	0.994[d]	0.055	[18]
2	Methanol, 298 K, CCl_4	0.452	0.184	5	0.999[e]	0.006	[19]
3	HNCS, 298 K, CCl_4	1.307	0.183	13	0.990	0.087	[21]
4	Phenol, 298 K, CCl_4	0.981	−0.087	11	0.996[f]	0.056	[20][22]
5	4-Chlorophenol, 293 K, C_6H_{12}	1.225	0.160	10	0.996[g]	0.024	[24]

[a] Number of common ethers. – [b] Correlation coefficient. – [c] Standard deviation. – [d] After excluding furan, Ph_2O, and nBu$_2$O. – [e] After excluding dioxane. – [f] After excluding tetrahydropyran. – [g] After excluding tBuOMe.

the medium is increased. It is important to note that the most shifted band is more sensitive to temperature variations, showing that the complex with the greatest $\Delta\nu$(OH) has also the greatest formation enthalpy, in agreement with the Badger-Bauer rule[32][33].

We assume geometries **A** and **B** shown in Figure 3 for the most stable and the least stable complexes, respectively. The geometry **A**, tetrahedral at the ether oxygen atom, i.e. with an OH group in the direction of a conventional sp^3 oxygen lone pair, has been found in the solid state for the pentafluorophenol−dioxane complex[34], and in the gas phase for the hydrogen-bonded dimers of oxetane, oxirane, or 2,5-dihydrofuran with various molecules HX[35][36][37]. However, a crystallographic analysis[38] of the directionality of hydrogen bonding to sp^3 oxygen atoms show that the preference for a hydrogen-bond donor group to align with the axes conventionally associated with the oxygen lone pairs is quite weak because it is readily masked by lattice forces and steric interferences between the R or R′ substituent and the OH group. Since most of the hydrogen bonds crystallographically surveyed do tend to lie within the plane of the two oxygen lone pairs, a trigonal geometry **B** is suggested for the second isomer.

Figure 3. Two possible structures for the complex ether−hydrogen-bond donor



We expect that complex **A** is more destabilized than **B** by bulky R and/or R′ groups and we indeed observe the following cyclic ethers. We also observe, from the relative intensities of OH bands attributed to complexes **A** and **B**, that the percentage of **B** increases from cyclic ethers to epoxides.

Structure−Hydrogen-Bond Basicity Relationships

The pK_{HB} scale of ethers extends from 1.44 for 2,3-diadamant-2-yloxirane, the most basic monoether, to −0.53 for hexamethyldisiloxane, the least basic one. Other weakly basic ethers are $(CF_3)_2$CHOMe (−0.41) and furan[*] (−0.40). These examples illustrate the importance of steric effects ($Me_3SiOSiMe_3$), resonance effects (furan) and field-inductive effects [$(CF_3)_2$CHOMe] on the hydrogen-bond basicity of sp^3 oxygen atoms.

The field-inductive effect can be rationalized by means of the field-inductive substituent constant σ_F[41]. For the series of acyclic non-conjugated ethers ROR′ (**1**−**8**, **10**, **11**, **13**, **16**, **17**, and **20**), the pK_{HB} values, corrected when necessary for the association on a second site, are correlated to the sum of the σ_F constants of substituents R and R′ (eq. 7).

$$pK_{HB} = 1.033 - 3.367\ \Sigma\sigma_F \quad (7)$$
$N = 14$; $r = 0.942$; $s = 0.18$

This correlation is rather satisfactory if we consider that steric, polarizability, and conformational effects are not taken into account by the σ_F parameter. The reaction constant ρ_F is significantly larger for ethers (3.37) than for esters RCOOEt (1.79)[11] or amides $RCONMe_2$ (2.74)[12], as expected for a direct substitution on the hydrogen-bond acceptor atom itself.

[*] Rotational spectroscopy shows[39] that HCl is hydrogen-bonded to the furan oxygen atom along the C_2 symmetry axis of the molecule. We expect that furan is also an oxygen base towards 4-fluorophenol (and not a π base as assumed in ref.[40]).

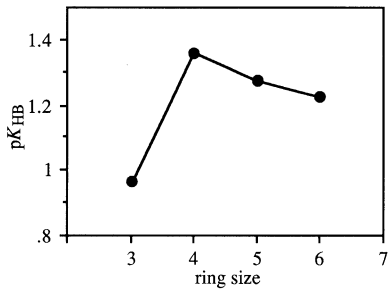
If we assume that the lower basicity of peroxides ROOR′ compared to ethers is mainly the consequence of the electron-withdrawing field-inductive effect of each oxygen atom on the other, and since the sum of the σ_F substituent constants of the alkyl R and of the alkoxy OR′ is equal to 0.25[41], we calculate from eq. (7): pK_{HB} = 0.16 for one oxygen atom and (adding log 2 = 0.30) 0.46 for the whole peroxide. This predicted value agrees very well with the experimental value (0.43) of *t*BuOO*t*Bu, but this agreement may be fortuitous since the prediction does not take into account the steric effects of the *t*Bu groups. On the contrary the predicted pK_{HB} of cyclic peroxides is by far too low when compared to the experimental values. We suspect that this difference originates in lone-pair−lone-pair repulsions between the two adjacent oxygen atoms. These repulsions are not taken into account by the σ_F constant and are more effective in cyclic than in acyclic peroxides where they can be released by rotation around the O−O bond. Lone-pair repulsions increase the basicity as described by Taft et al. for adjacent nitrogen atoms[42].

The importance of steric effects on the hydrogen-bond basicity of ethers is well established[24] and explains that the most crowded ether *t*Bu$_2$O is the least basic of alkyl ethers. However, West et al.[20] have shown that chain branching α to the oxygen atom has two opposite effects. It increases the hydrogen-bond formation enthalpy because of the electronic effects of alkyl groups and this should increase basicity in the order: Me < Et < *i*Pr < *t*Bu. It also increases the hydrogen-bond formation entropy because of the steric effect and this should reduce basicity in the order: Me > Et > *i*Pr > *t*Bu. The pK_{HB} sequence: *t*BuO*t*Bu < *t*BuOEt < *t*BuOMe corresponds to the predominance of the steric effect, but in the following order: *t*Bu$_2$O < Et$_2$O < *i*Pr$_2$O the second inequality corresponds to the predominance of electronic effects over the steric effect. The severe steric requirement of two SiMe$_3$ groups also explains, but not totally (vide infra), the very low basicity of (Me$_3$Si)$_2$O.

The electron-withdrawing resonance effect of the vinyl and ethynyl groups adds to their electron-withdrawing field-inductive effect for explaining the low basicity of EtOCH=CH$_2$ and EtOC≡CH. A transfer of p_π electrons from the oxygen atom to the d_π orbitals of the silicon atoms[43] also reduces the oxygen basicity of (Me$_3$Si)$_2$O.

As seen in Figure 4, the hydrogen-bond basicity of cyclic ethers varies with the ring size in the following order: 4- > 5- > 6- > 3-membered rings.

Figure 4. Variation of pK_{HB} with the ring size of cyclic ethers



This non monotonic variation of pK_{HB} with the ring size might be the result of two opposite effects. When the C−O−C angle diminishes with the ring size, the steric hindrance of the oxygen lone pairs by the α-methylene groups must decrease[24], and consequently pK_{HB} increases. But oppositely the closure of the C−O−C angle must increase the s character of the oxygen lone pairs[17][20] reducing pK_{HB}. The rehybridization of the oxygen lone pairs might be significant mainly in epoxides[20] and this would explain that the three-membered ring structure causes a definite decrease in basicity.

The pK_{HB}-Δν(OH) Relationship

The correlation between the Gibbs energies of hydrogen-bond formation (i.e. pK_{HB}) and infrared shifts has often been studied. It is well established[18] that a general correlation does not exist for all kinds of bases, but that family-dependent relationships do hold[7][8][9][10][11][12][14][15] if a number of conditions are obeyed. In this context, a family is defined as a group of bases that possess the same hydrogen-bond acceptor atomic center in roughly the same hybridization state. It has been observed that the various families of bases trace roughly parallel lines in the pK_{HB},Δν(OH) plane, disposed from left to right with the increasing p character of the hydrogen-bond accepting lone pair(s)[7b]. In other words, for the same pK_{HB} value Δν(OH) increases from nitriles (sp N) to pyridines (sp^2 N) and to amines (sp^3 N).

The conditions for a good family-dependent Δ*G*-Δν relationship to be observed are the following. Firstly, the steric requirements of the hydrogen-bond acceptor site must remain almost constant. Secondly, the hydrogen-bond acceptor site must remain unique; if not, the pK_{HB} must be corrected (by the statistical factor −log *n* if there are *n* equivalent sites). In any case, and at last, these sites must not be adjacent, because lone-pair(s)−lone-pair(s) repulsions increase more importantly pK_{HB} than Δν(OH)[44]. Ethers and peroxides constitute interesting groups of bases for checking these rules and for showing how the pK_{HB}-Δν(OH) plot reveals or confirms structural features governing the hydrogen-bond basicity. Since methanol gives more symmetrical absorptions (vide supra) leading to more accurate Δν values, $\Delta\nu_1$(OH) is preferred to $\Delta\nu_2$(OH) for this plot.

In the pK_{HB} vs. $\Delta\nu_1$(OH) plot (Figure 5), we observe a scattering of points, and calculate a very low correlation coefficient (r = 0.692, n = 40). In applying to pK_{HB} the polysites corrections (eqs. 4 et 5), we improve significantly the correlation coefficient (r = 0.80). The remaining scatter is partly caused by steric effects to which the Δ*G*-Δν correlation is very sensitive[*]. In order that they do not obscure other structural effects, we have focused on cyclic ethers and peroxides, which are less dependent on steric effects than

[*] For the reason that Δ*G* is more sensitive to steric effects, through its entropic term, than Δν, roughly related to Δ*H*, according to the Badger-Bauer relationship[32][33].

open-chain ethers since cyclization pulls back the alkyl chains.

Figure 5. Family-dependent relationship between pK_{HB} and $\Delta\nu_1(OH)$ for cyclic ethers; numbers refer to Table 1

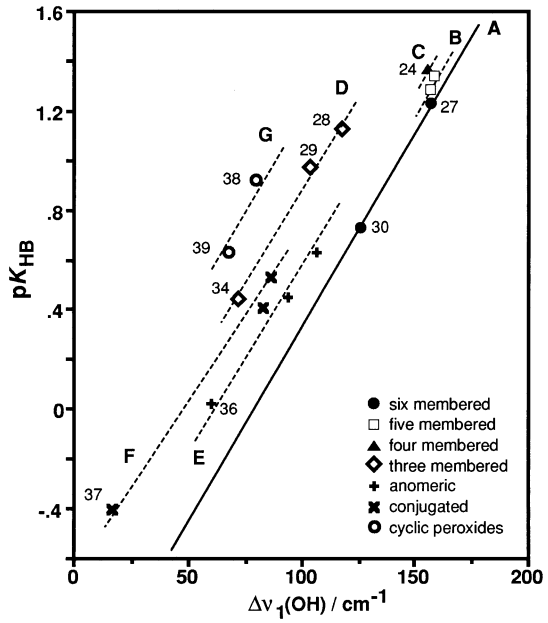


Figure 5 clearly shows:

1) Separate lines A−D for six-, five-, four-, and three-membered rings ranging from right to left when the oxygen lone pairs gain s character with the closure of the C−O−C angle.

2) A line E for 1,3,5-trioxane, 1,3-dioxane, and 1,3-dioxolane, cyclic ethers where the 1,3 positions of the oxygen atoms allow the anomeric effect[45] to operate.

3) A line F for conjugated cyclic ethers. Such conjugation of the oxygen lone pairs with a π system represents a partial rehybridization giving larger s character to the lone pairs. Consequently, the line F is situated on the left side of lines A and B.

4) The position of cyclic peroxides at the upper limit of the plot (line G), confirming that lone-pairs−lone-pairs repulsion of the adjacent oxygen atoms increases pK_{HB}.

5) A rough parallelism of lines A−F.

Now steric effects appear clearly as deviations under the appropriate lines. If we refer open-chain ethers to the line A of unstrained rings, the deviations collected in Table 4 represent a rough estimation of the steric effect in some crowded ethers.

Table 4. Vertical deviations (Δ) of some acyclic ethers and a peroxide from the line A of Figure 5 corresponding to the unstrained rings

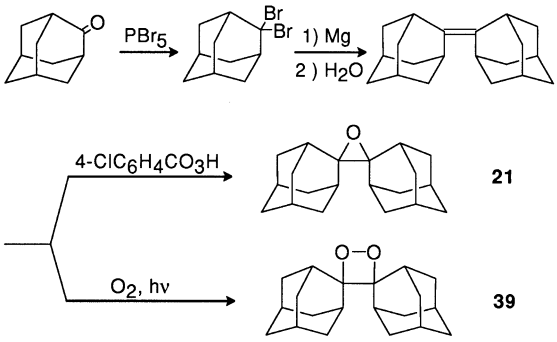
Compound	Δ	Compound	Δ
Et−O−Et	−0.11	*t*Bu−O−Et	−0.28
$PhCH_2-O-CH_2Ph$	−0.13	*n*Bu−O−*n*Bu	−0.30
$ClCH_2CH_2-O-Et$	−0.15	$Me_3Si-O-SiMe_3$	−0.50
*t*Bu−O−Me	−0.19	*t*Bu−O−*t*Bu	−0.66
*i*Pr−O−*i*Pr	−0.23	*t*Bu−O−O−*t*Bu	−0.20

Finally, we note in Table 4 that *t*BuO−O*t*Bu behaves similarly as hindered ethers. This confirms that the conformational flexibility of acyclic peroxides allows a significant release of the lone-pairs interactions between the adjacent oxygen atoms, unlike the cyclic peroxides.

Experimental Section

Materials: Most compounds were purchased from Aldrich. Their purity was checked by gas chromatography and, when necessary, they were distilled, and dried over molecular sieves. 4-fluorophenol was sublimed over P_2O_5 at 60°C and 13 Pa. Spectroscopic-grade CCl_4 was passed through a column of freshly activated 4-Å molecular sieves before use. Spectroscopic-grade methanol was kept over 3-Å molecular sieves. − Ascaridole (**38**) and $MeOCH(CF_3)_2$ (**20**) have been generously given to us by D. G. Morris (Glasgow) and M. H. Abraham (London), respectively. Di-*tert*-butyl ether (**8**) was synthesized in the laboratory of Prof. C. Reichardt (Marburg) according to the method of Erickson and Ashton[28]. Diadamantyloxirane **21** and diadamantyldioxetane **39** have been synthetized by J.-Y. Le Questel in the department of chemistry of the University of Glasgow under the supervision of D. G. Morris according to the procedure shown in Figure 6. Details of the preparations and physical properties of **21** and **39** have been reported in the Le Questel thesis[29].

Figure 6. Synthetic pathway for compounds **21** and **39**



Infrared Spectra: Infrared measurements were carried out with Bruker IFS 48 or Nicolet 510 M FTIR instruments, selecting a 1-cm^{-1} resolution and an accumulation of 256 scans. The 1-cm (for the absorbance measurements) and 4-cm (for the shifts measurements) cells were thermostatted at 25 ± 0.2°C. Variable-temperature experiments were performed from −6 to +55°C with a Peltier system. All operations, including the filling of the cells, were conducted in the dry atmosphere of a glove box. The spectra were treated with softwares including deconvolution and mathematical decomposition of overlapping or dissymetrical bands into Gauss-Lorentz-type components.

Equilibrium Constants: The formation constant of 1:1 complexes (c) of 4-fluorophenol (a) with bases (b) is defined as $K_f = C_c/C_a \cdot C_b$ where the equilibrium concentrations are on a molar scale. The initial molar concentration of 4-fluorophenol, C_a^0, was kept under the limit of $3 \cdot 10^{-3}$ mol l^{-1} in order to prevent self-association, while the initial molar concentration of the base, C_b^0, was adjusted so that the complexation of 4-fluorophenol was not less than 20% and not more than 80%. For example, for 2-methyltetrahydrofuran (K_f = 21.8 l mol^{-1}), C_b^0 was varied from $1.4 \cdot 10^{-2}$ mol l^{-1} (23% of the phenol is complexed) to $5.6 \cdot 10^{-2}$ mol l^{-1} (53% of the phenol is complexed). The equilibrium concentration C_a was obtained from the absorbance of the 3614 cm^{-1} band of 4-fluorophenol (ε =

237 l mol^{-1} cm^{-1}) and the other equilibrium concentrations were deduced from C_a. The maximum error in pK_{HB} is estimated to be ± 0.04.

In the case of polyethers, we must maintain the ether concentration at least in tenfold excess, in order to favor the formation of 1:1 complexes over *n*:1 complexes. The constancy of the equilibrium constants determined at different ether concentrations on the basis of 1:1 complex formation, indicates that the 1:1 complex is the primary species formed (Table 5).

Table 5. Variation of K_f (l mol^{-1}) as a function of C_b^0/C_a^0 for the 4-fluorophenol/18-crown-6 complex; K_f is constant when the ratio C_b^0/C_a^0 is over 10

C_b^0/C_a^0	0.42	0.85	1.73	3.36	7.15	10.7	13.7	15.8
K_f	142	131	122	114	97.1	95.9	95.7	95.8
	1:1, 2:1, ... complexes[a]				1:1 complexes: K_f = 95.8			

[a] By assuming the presence of only a 1:1 complex and a 2:1 complex (2 molecules of 4-fluorophenol for 1 crown ether), we obtain, by the Huyskens method[30], K_f(1:1) = 93.7 l mol^{-1} in good agreement with the value obtained when the crown ether is in tenfold to sixteenfold excess.

Infrared Shifts: The wavenumber shifts of the OH bands of methanol at 3644 cm^{-1} and 4-fluorophenol at 3614 cm^{-1} are defined as $\Delta\nu_1(OH) = 3644 - \nu_1(OH\cdots O)$ and $\Delta\nu_2(OH) = 3614 - \nu_2(OH\cdots O)$, respectively. They are known to ± 2 cm^{-1} if the $\nu(OH\cdots O)$ band is almost symmetrical, but asymmetry and mathematical decomposition cause larger errors.

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