Hydrogen-bond Basicity of Nitro-compounds

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The hydrogen bond basicity scale pK_{HB} (logarithm of the formation constant of 4-fluorophenol–base complexes in CCl_4) has been measured for nitro-compounds. This thermodynamic basicity scale is correlated to a spectroscopic basicity scale. The Yukawa–Tsuno equation is obeyed in the nitroaromatics. We have shown that nitroenamines are the most basic nitro-compounds presently known and have hydrogen bond basicity comparable to tributylamine.

We are currently assembling a thermodynamic hydrogen bond basicity scale based on pK_{HB}, the logarithm of the formation constant K_{HB} of the 4-fluorophenol–base 1 : 1 complex in CCl_4 at 298 K [reaction (*a*) and eqn. (1)]. In the equilibrium (*a*) 4-fluorophenol is a reference hydrogen bond donor chosen for technical reasons.[1]

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

$$K_{HB} = [\text{Complex}]/[B][4\text{-}FC_6H_4OH]; \quad pK_{HB} = \log_{10} K_{HB} \qquad (1)$$

We have already studied amidines,[2] alcohols,[3] nitriles,[4] amides[5] and esters.[6] We present here our pK_{HB} scale for nitro-compounds. A very limited number of studies[7] have investigated hydrogen-bonding of alcohols and phenols with nitro-compounds. However nitroparaffins are of great industrial importance as explosives, solvents or reactants, nitroaromatics are often used as probes of solvent polarity[8] and the nitro-group participates in the structure of important antibiotics, insecticides, fungicides or herbicides.[9]

We have measured nine primary pK_{HB} values, and used these to calculate five secondary values from linear free energy relationships[10] and linear correlations between pK_{HB} and $\Delta\nu(OH)$, the lowering of the $\nu(OH)$ frequency of 4-fluorophenol, or methanol, on going from the free to the hydrogen bonded OH group. Both primary and secondary values can be transformed into an entirely equivalent, but more convenient, scale through eqn. (2).[10]

$$\beta_2^H = (pK_{HB} + 1.1)/4.636 \qquad (2)$$

Experimental

Except *N*-nitrocamphorimine[11] and 1-piperidino-2-nitroethylene[12] synthesized in our laboratories, the chemicals used were commercial.

The FTIR spectroscopic method for measuring hydrogen bond formation constants has been described previously.[4] Values of pK_{HB} are probably accurate to better than ±0.03. The concentrations of nitro-compounds and 4-fluorophenol are chosen such as only 1 : 1 complexation is possible.

IR measurements were carried out with a Fourier-Transform spectrometer Bruker IFS 45 by selecting 1 cm^{-1} resolution. A 1 cm quartz infrasil cell was thermostatted at 25 ± 0.2 °C. All the measurements were performed in CCl_4.

The frequency shifts of the OH band of methanol at 3644 cm^{-1} and 4-fluorophenol at 3614 cm^{-1} are defined as $\Delta\nu_2 = 3644 - \nu_2(OH\cdots)$ and $\Delta\nu_1 = 3614 - \nu_1(OH\cdots)$, respectively. They are believed to be accurate to within ± 1–5 cm^{-1}.

Results

The pK_{HB}, IR frequency shifts $\Delta\nu_1(OH)$ and $\Delta\nu_2(OH)$, and β_2^H are reported for the primary set in Table 1. Our experimental pK_{HB} value for nitrobenzene (0.30) disagrees with the statistical values 0.48 (ref. 10) and 0.73 (ref. 13) previously reported in the literature.

The correlation coefficient, *r*, and the standard deviation, *s*, show that excellent correlations exist between pK_{HB} and $\Delta\nu_2(OH)$ [eqn. (3)] or $\Delta\nu_1(OH)$ [eqn. (4)] for nine compounds.

$$pK_{HB} = 1.716[\Delta\nu_2(OH)/100] - 0.13 \qquad (3)$$
$$n = 9 \quad r = 0.9995 \quad s = 0.02$$

$$pK_{HB} = 0.994[\Delta\nu_1(OH)/100] - 0.49 \qquad (4)$$
$$n = 9 \quad r = 0.9987 \quad s = 0.03$$

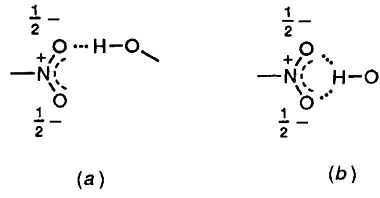
Both equations (3) and (4) can safely be used for calculating secondary pK_{HB} values for nitroethane $EtNO_2$ and 2-methyl-2-nitropropane Bu^tNO_2 for which only $\Delta\nu(OH)$ has been measured. The results are reported in Table 2. Secondary pK_{HB} values can also be calculated from the formation constants for the complexes of nitroaromatics with *p*-nitrophenol measured by Su and Hong.[14] The linear free energy relationship (5)

$$\log K = 1.299\, pK_{HB} + 0.328 \qquad (5)$$

established by Abraham *et al.*[10] between pK_{HB} and log *K* for *p*-nitrophenol complex permits the calculation of three new secondary pK_{HB} values reported in Table 2.

Discussion

Hydrogen Bonding Site.—Concentrations chosen imply that we have formed 1 : 1 complexes but we do not know if the hydrogen bond that has been created is (*a*) two- or (*b*) three centred.*



(*a*) (*b*)

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* We thank a referee for informing us that (*b*) has been found in the solid state. (T. W. Panunto, Z. Urbânczyk-Lipkowska, R. Johnson and M. C. Etter, *J. Am. Chem. Soc.*, 1987, **109**, 7786.)

Table 1 Frequency shifts (cm^{-1}), $\Delta\nu_1$(OH), of 4-fluorophenol and $\Delta\nu_2$(OH) of methanol, and primary pK_{HB} and β_2^H values for nitro-compounds

No.	Compound	Formula	$\Delta\nu_2$	$\Delta\nu_1$	pK_{HB}[b]	$\beta_2^{H\,b}$
1	Nitromethane	$MeNO_2$	22	77	0.27	0.30
2	Nitrobenzene	$PhNO_2$	26	84	0.30	0.30
3	*N*-Nitrocamphorimine	$C_{10}H_{16}N\text{-}NO_2$	28	82	0.34	0.31
4	2-Nitropropane	Pr^iNO_2	30	86	0.41	0.33
5	4-Nitro-*o*-xylene	$Me_2C_6H_3NO_2$	35	93	0.46	0.34
6	4-Nitroanisole	$MeOC_6H_4NO_2$	38	101	0.50	0.35
7	*N*,*N*-Diethyl-4-nitroaniline	$Et_2NC_6H_4NO_2$	60	138	0.90	0.43
8	1-Dimethylamino-2-nitroethylene[a]	$Me_2NCH{=}CHNO_2$	93	197	1.47	0.55
9	1-Piperidino-2-nitroethylene[a]	$\underline{CH_2(CH_2)_4}NCH{=}CHNO_2$	98	205	1.55	0.57

[a] These compounds exist solely in the *E*-form.[19] [b] In the hypothesis of a two-centre hydrogen bond these values must be corrected by the statistical factor log 2 on pK_{HB}.

Table 2 Hydrogen bond basicity of nitro-compounds: frequency shifts (cm^{-1}) and secondary pK_{HB} and β_2^H values

No.	Compound	Formula	$\Delta\nu_2$	$\Delta\nu_1$	pK_{HB}[c]	$\beta_2^{H\,c}$
10	Nitroethane	$EtNO_2$	29	81	0.32[a]	0.31
11	2-Methyl-2-nitropropane	Bu^tNO_2	31	92	0.42[a]	0.33
12	4-Nitrotoluene	$MeC_6H_4NO_2$	—	—	0.35[b]	0.31
13	4-Chloronitrobenzene	$ClC_6H_4NO_2$	—	—	0.22[b]	0.28
14	3-Chloronitrobenzene	$ClC_6H_4NO_2$	—	—	0.13[b]	0.26

[a] Calculated by eqn. (4). [b] Calculated by eqn. (5). [c] In the hypothesis of a two-centre hydrogen-bond these values must be corrected by the statistical factor log 2 on pK_{HB}.

The possibility of two 1 : 1 complexes exists for compounds **3** and **6**–**9** since ether oxygen, imine nitrogen and amino nitrogens are potential hydrogen bond acceptor atoms in these bifunctional compounds. The observation of one symmetric ν(OH • • •) band suggests that one complex is formed. The excellent relationships between pK_{HB} and $\Delta\nu$(OH) show that the preferred site of hydrogen bonding in the nitro-compounds shown in Table 1 is the nitro group common to all nine compounds.

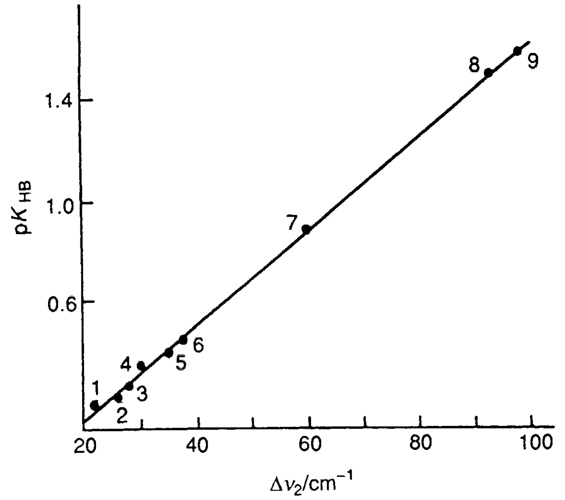

Fig. 1 Relation of the thermodynamic hydrogen bond basicity scale, pK_{HB}, with a spectroscopic basicity scale, the IR shift $\Delta\nu_2$ of the OH vibrator of methanol. Numbers refer to Table 1.

This conclusion agrees with chemical intuition that in the push–pull compounds **6**–**9**, the pulling nitro-group, enriched with electrons, is a better hydrogen bond centre than the pushing ether oxygen in **6** or amino nitrogens in **7**–**9**, electron-impoverished. For the *N*-nitrocamphorimine **3**, the loss of hydrogen bond basicity of the imino nitrogen by virtue of the strong electron-withdrawing field effect of the nitro group (σ_F = 0.65)[15] is in line with results[16] on an imino nitrogen, substituted by a weaker electron-withdrawing CH_2CN group (σ_F = 0.32),[15] having no measurable hydrogen-bond basicity.

Substituent Effects in Nitrobenzenes.—In *meta*- and/or *para*-substituted nitrobenzenes, the electronic effects of substituents 3-Cl, 4-Cl, H, 4-Me, 3,4-Me$_2$, 4-OMe and 4-NEt$_2$ on the hydrogen bond basicity can be analysed by means of the Yukawa–Tsuno eqn. (6)[17] where p$K°_{HB}$ refers to nitrobenzene,

$$\mathrm{p}K_{HB} = \mathrm{p}K^{\circ}_{HB} + \rho(\sigma^{\circ} + r\Delta\sigma^{+}) \qquad (6)$$

$\sigma°$ is the normal substituent constant,[17] $\Delta\sigma^+$ measures the through-conjugation effect of π-donor substituents[17] and the regression coefficients ρ and r measure the sensitivity of hydrogen bond basicity to these effects. Eqn. (7) is obtained and

$$\mathrm{p}K_{HB} = 0.295 - 0.439\,(\sigma^{\circ} + 0.548\Delta\sigma^{+}) \qquad (7)$$
$$n = 7 \quad r = 0.996 \quad s = 0.03$$

shows excellent statistics for the above compounds and enables a prediction to be made of the hydrogen bond basicity of numerous nitrobenzenes and, particularly, the contribution of the nitro-group to the total hydrogen bond basicity of polybasic nitrobenzenes such as nitrobenzonitriles, ethyl nitrobenzoates or nitroacetophenones.

Nitroaniline and Nitroenamines.—The most basic nitrobenzene is the push–pull compound 4-$Et_2NC_6H_4NO_2$, in which the pushing NEt$_2$ substituent and the pulling NO$_2$ function are separated by the phenylene transmitter. We have previously found that the replacement of the phenylene group by a vinyl group, increases strongly the hydrogen bond basicity of nitriles[18] and esters.[6] The same situation is found in the nitro family: the nitroenamines **8** and **9** are more basic respectively by 0.57 and 0.65 pK_{HB} unit than the nitroaniline **7**, and accordingly become the strongest hydrogen bond nitro-bases presently known. Again, vinylogy produces ‘super-basic’ compounds,*

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* Our finding on the base-enhancing effects of vinylogy has been anticipated in ref. 20.

reinforced by the finding that 1-piperidino-2-nitroethylene has an hydrogen bonding basicity comparable to that of tributylamine ($pK_{HB} = 1.57$).[1]

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