Hydrogen Bonding of Neutral Species in the Gas Phase: The Missing Link

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Using our new FTIR data[1] and eight values from the literature, a set of 31 equilibrium constants, $K_c(g)$, for the 1:1 hydrogen bond (HB) association between neutral HB donors, A–H, and acceptors, B (reaction 1), at 295 K has been constructed that spans 6 orders of magnitude. This data set has allowed us to carry out what we believe to be the first systematic treatment of the influence of the structures of these species on the thermodynamic stability of their 1:1 complexes in the gas phase. This study was prompted by our interest in developing a unified treatment of structural effects on the thermodynamic stability of 1:1 HB complexes in solution and in the gas phase.

$$A-H(g) + B(g) \rightleftarrows A-H\cdots B(g) \qquad K_c(g) \qquad (1)$$
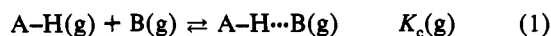
Presently available techniques[2-5] have allowed the determination of a large number of equilibrium constants for 1:1 HB associations between ions and molecules in the gas phase.

Thousands of equilibrium constants, K_c, for 1:1 associations between neutral species in "inert" solvents S, (mostly tetrachloromethane and cyclohexane) reaction 2, are also known.[7] The

$$A-H + B \overset{S}{\rightleftarrows} A-H\cdots B \qquad (2)$$
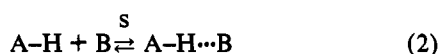
simplest empirical expression of K_c in terms of descriptors of the HB donor abilityof A–H and the HB acceptor ability of B in solution in CCl₄ at 25 °C is eq 3,[8] wherein α_2^H and β_2^H are

$$\log K_c(CCl_4) = 7.354\alpha_2^H\beta_2^H - 1.094 \qquad (3)$$

descriptors of the HB "acidity" and "basicity" of A–H and B, respectively. This expression successfully applies to thousands of systems.[9] The empirical[10a] and quantum-mechanical treatments[10b,c] of these descriptors yield valuable information on

the structural factors determining the stability of 1:1 HB complexes and on the nature of HB interactions. As regards neutral species, it is important to ascertain whether the α_2^H and β_2^H parameters reflect truly "intrinsic" properties of HB donors and acceptors or else involve a mixture of intrinsic properties and solvation effects.[11] It also remains to be determined if bilinear expressions such as eq 3 also apply *generally* to HB associations involving ionic species in solution.

A new experimental method,[1] based on Fourier transform infrared spectrometry (FT IR) has been developed that overcomes many of the important experimental difficulties (mostly due to adsorption and condensation phenomena) inherent to the determination of the equilibrium constants, $K_c(g)$, for reaction 1a in the gas phase. Briefly stated, this method involves the treatment by spectral substraction techniques of the FT IR absorption spectra (4000–400 cm⁻¹) of series of mixtures (AH(g), B(g), AH⋯B(g)). A statistical procedure leads to the simultaneous determination of the absorptivity of the complex (at any wavelength within the observed spectral range) and the equilibrium constant $K_c(g)$, through the combination of the spectral data with the experimental values of the partial pressures of AH and B and the total pressures of the mixtures. On the basis of reproducibility, the relative uncertainty on K_c values is estimated at ca. 10%.[1]

Using this method,[1] 23 $K_c(g)$ values were obtained for systems involving a substantial variety of HB donors and acceptors. These results, together with eight values taken from the literature, are collected in Table 1. They span a range of ca. 7.1 kcal·mol⁻¹ in Gibbs energy. Data for the dimerization of alcohols and water were mostly obtained by nonspectroscopic methods and are taken from the literature. As shown by inspection of Table 1 (see also ref 13), their uncertainties are quite substantial. This notwithstanding, they are very important, for they allow the extension of the range of $K_c(g)$ values. Most of the FT IR data[1] were obtained at 22.0 ± 0.1 °C. In a few cases (indicated in Table 1), temperatures were slightly different. $K_c(g)$ values were corrected by means of the enthalpies for reaction 1.[24]

By analogy with the methodology followed in the study of similar systems in CCl₄ solutions, the relationship between log $K_c(g)$ and the product $\alpha_2^H\beta_2^H$ was explored and eq 4 was found to hold quite satisfactorily, where n (number of data points) = 23; r (correlation coefficient) = 0.987; sd (standard deviation of fit) = 0.20 log units. Standard deviations on the calculated coefficients

$$\log K_c(g) = 9.13 \ (0.32) \ \alpha_2^H\beta_2^H - 0.87 \ (0.11) \qquad (4)$$

are given in parentheses. It is of interest that, while K_c values

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(24) Taken from data in ref 7a for the same or cognate compounds.

Table 1. Equilibrium Constants at 22.0 °C for Reaction 1a in the Gas Phase

A–H	B	$K_c(g)^a$	$K_c(g)^a$ av	ref	α_2^H (A–H)^b	β_2^H (B)^c
H_2O	H_2O	0.92		12, 13		
		1.8	1.2	13, 14	0.35	0.38
		0.97		13, 15		
CH_3OH	CH_3OH	1.5		16, 13		
		1.5		14b, 13		
		1.8	1.6	17, 13	0.37	0.41
		1.5		18, 13		
		1.9		19, 13		
	$(CH_3)_3N$	19	19	1	0.37	
C_2H_5OH	C_2H_5OH	1.9		19, 13		
		2.4	2.5	17, 13	0.33	0.44
		3.3		18, 13		
$i\text{-}C_3H_7OH$	$i\text{-}C_3H_7OH$	7.6		18, 13		
		2.9		17, 13		
		2.6	4.0	20, 13	0.32	0.47
		2.8		21, 13		
$t\text{-}C_4H_9OH$	$t\text{-}C_4H_9OH$	7.8		13, 18		
		4.3	6.1	22, 13	0.32	0.49
C_4H_5N (pyrrole)	$(CH_3)_3N$	29	29	1	0.41	
CF_3CH_2OH	C_2H_5CHO	21^d	21	1	0.57	0.22
	CH_3OH	24	24	13	0.57	0.23
	$(C_2H_5)_2O$	38^e	38	1	0.57	0.26
	$(CH_3)_2CO$	53	53	1	0.57	0.28
	C_4H_8O (THF)	82	82	1	0.57	0.51
	NH_3	56	56	1	0.57	
	C_5H_5N	1.9×10^2	1.9×10^2	1	0.57	0.62
	$(CH_3)_3N$	$4.0 \times 10^{2}\,^f$	4.0×10^2	1	0.57	
	$(C_2H_5)_3N$	2.9×10^2	2.9×10^2	1	0.57	0.67
	$[(CH_3)_2N]_2C{=}NH$	3.8×10^3	3.8×10^3	1	0.57	0.91
$(CF_3)_2CHOH$	CH_3OH	85	85	18b	0.77	0.41
	$(C_2H_5)_2O$	$1.8 \times 10^{2}\,^g$	$1.8 \times 10^{2}\,^g$	1	0.77	0.45
	$(CH_3)_2CO$	2.5×10^2	2.5×10^2	1	0.77	0.50
	C_4H_8O (THF)	5.6×10^2	5.6×10^2	1	0.77	0.51
	NH_3	5.8×10^2	5.8×10^2	1	0.77	
	$(CH_3)_3N$	8.1×10^3	8.1×10^3	1	0.77	
	$(C_2H_5)_3N$	3.8×10^3	3.8×10^3	1	0.77	0.67
$(CF_3)_3COH$	$(CH_3)_2O$	4.9×10^2	4.9×10^2	23	0.86	0.43
	$(C_2H_5)_2O$	6.8×10^2	6.8×10^2	1	0.86	0.45
	$(CH_3)_2CO$	1.1×10^3	1.1×10^3	1	0.86	0.50
	C_4H_8O (THF)	3.8×10^3	3.8×10^3	1	0.86	0.51
	NH_3	5.1×10^3	5.1×10^3	1	0.86	
	$(CH_3)_3N$	1.6×10^5	1.6×10^5	1	0.86	
	$(C_2H_5)_3N$	3.4×10^4	3.4×10^4	1	0.86	0.67

^{a} In mol^{-1}·L. ^{b} Taken from ref 9b. ^{c} Taken from ref 9a. ^{d} Original experiment performed at 25.0 °C. ^{e} Original experiment performed at 28.0 °C. ^{f} Original experiment performed at 23.0 °C. ^{g} Original experiment performed at 25.0 °C.

vary by about 6 powers of 10, it is only in two cases that departure from the behavior predicted by eq 4 reaches 0.3 log units.

Data for the associations involving NH_3 and $N(CH_3)_3$ were not included in this correlation. Instead, eq 4 was used to determine β_2^H values for these compounds. The computed values, respectively 0.53 and 0.69, are in excellent agreement with the latest determinations in CCl_4 solution by Laurence and Berthelot.[25]

Although future work might lead to a slight modification of the coefficients in eq 4, the following important conclusions can be safely drawn:

1. The bilinear formalism that succeeds in CCl_4 solution also applies to HB equilibria in the gas phase.

2. Hence, for neutral molecules, *there is a general, "intrinsic" pattern of HB reactivity that is common to 1:1 interactions in the gas phase and in solution (in the absence of specific solvent-solute interactions).*

3. The independent terms in eq 3 and 4 are very close, −0.87 and −1.10, respectively. This is relevant, because for $\alpha_2^H\beta_2^H = 0$, log K_c = −1.10 in CCl_4 was considered to define the onset of

(25) Private communication from Profs. C. Laurence and M. Berthelot.

"true" HB interactions.[8a,9a,b] The fact that this value is practically the same in the gas phase, strongly supports this concept.

4. The ratio of the sensitivities to structural effects, namely, $9.13/7.35 = 1.24$, provides a quantitative measure of the attenuation of "true" HB effects on going from the gas phase to CCl_4 solution. Furthermore, from eq 3 and 4 we derive eq 5 (uncertainties on the coefficients are assumed to be those originating in eq 4. For small $\alpha_2^H\beta_2^H$ values and because of the

$$\log K_c(g) - \log K_c(CCl_4) = 1.78\ (0.32)\ \alpha_2^H\beta_2^H + 0.23\ (0.11)$$
$$(5)$$

combined uncertainties, equilibrium constants in the gas phase and in CCl_4 are quite comparable (within a factor of 2). As $\alpha_2^H\beta_2^H$ increases, so does the gap between log $K_c(g)$ and log $K_c(CCl_4)$. This likely reflects the increasing importance of the dielectric effect of the solvent.