under 50 atm of ethylene for 48 h at room temperature. The resulting mixture is then distilled at reduced pressure to separate $Fe(CO)_5$ from $Fe(CO)_4(C_2H_4)$. The fraction of interest is collected at 34 °C and 12 torr. The IR spectrum confirms the absence of $Fe(CO)_5$. $Fe(CO)_4(C_2H_4)$ is stored at −78 °C in the dark.

For the kinetic experiments, samples are prepared on a standard, all glass high-vacuum line. Gas mixtures are prepared by the pile-on method. Typically the reagent pressures are 0.050 torr of $Fe(CO)_4(C_2H_4)$, 1.5–9.0 torr of CO (research grade, Matheson), and 100–800 torr of ethylene (CP grade, Matheson). Ethylene is purified by 3 freeze–pump–thaw cycles to remove volatile impurities. The photolysis source is a Lambda-Physik EMG-101 Excimer Laser used on either the XeF (351 nm) or N_2 (337 nm) lines. All kinetic runs use 337 nm. The FTIR spectrometer is an IBM Model IR 98. Typically the spectra are taken at 0.5-cm^{-1} resolution, averaging 10 scans. The ethylene and CO spectra are subtracted out. The temperature in all experiments is ambient (297 K).

Acknowledgment. We thank C.G. Brinkley and M.S. Wrighton for communicating their results prior to publication. Acknowledgment is made to the Donors of the Petroleum Research Fund, administered by the American Chemistry Society, for support of this research.

Registry No. $Fe(CO)_3(C_2H_4)_2$, 74278-01-6; $Fe(CO)_3(C_2H_4)$, 84520-95-6; C_2H_4, 74-85-1; CO, 630-08-0.

Hydrogen Bonding as a Probe of Electron Densities: Limiting Gas-Phase Nucleophilicities and Electrophilicities of B and HX

A. C. Legon*[†] and D. J. Millen*[‡]

Contribution from the Department of Chemistry, University of Exeter, Exeter EX4 4QD, England, and Christopher Ingold Laboratories, Department of Chemistry, University College London, London WC1H OAJ, England. *Received July 7, 1986*

Abstract: Hydrogen-bond stretching force constants (k_σ) determined from the rotational spectra of dimers B···HX have been used to establish the nucleophilicities (N) of B for B = N_2, CO, PH_3, H_2S, HCN, CH_3CN, H_2O, and NH_3 and the electrophilicities (E) of HX for X = F, Cl, CN, Br, C≡CH, and CF_3. Values of E and N have been used to predict k_σ for a number of dimers as yet unobserved.

I. Introduction

Chemists have long recognized the desirability of predicting the strength of binding in a hydrogen-bonded dimer B···HX (or other weakly bound species) from the properties of the component molecules B and HX. In this article, we show how to establish limiting, gas-phase nucleophilicities (N) and electrophilicities (E) of the components B and HX in a simple manner from a readily determined spectroscopic property, namely, the hydrogen-bond stretching force constant, (k_σ). The quantities N and E can then be used to predict the strength of binding (as measured by the force constant k_σ) for a large number of dimers. The theoretical foundation of this procedure is discussed in terms of recent electrostatic modeling of the hydrogen bond.

As a result of the investigation of a large number of hydrogen-bonded dimers by rotational spectroscopy,[1] it has become possible to enunciate some simple, essentially electrostatic rules for predicting the angular geometries of dimers.[2] In particular, at equilibrium the HX molecule lies along the axis of a nonbonding electron pair on B. In more general terms, we might speak of the most electrophilic site of HX (i.e., the H atom) seeking the most nucleophilic site of B, but of course the nucleophilic end of HX will avoid this site on B. (We are thus using the terms *nucleophilicity* and *electrophilicity* in the etymologically exact sense. The electrophilicity of the H atom in HX is therefore a measure of its capacity to seek out a particular (unperturbed) electron-rich region on a standard molecule B. We have deliberately used the qualification "limiting" in discussing E and N to draw attention to the fact that they are derived from measurements in weakly bound dimers and that this usage therefore differs from the more common but less literal view of the terms which is restricted to the extreme case of group transfers during chemical reaction.) The electrostatic approach to hydrogen bonding has received a quantitative interpretation by Buckingham and Fowler[3] who use a distributed multipole analysis to predict angular geometries. Rotational spectroscopy, as well as leading to geometries, has also provided hydrogen-bond stretching force constants (k_σ) for many dimers B···HX.[4] A comparison of k_σ values within a series gives a measure of the relative strength of the dimers which are, moreover, in isolation in the gas phase. It is timely to interpret the k_σ values in terms of the properties of the individual components B and HX in a way that employs an analogous approach to that used for angular geometries, i.e., the concepts of nucleophilicity and electrophilicity.

II. Limiting, Gas-Phase Nucleophilicities and Electrophilicities.

The success of the nonbonding electron-pair model in predicting angular geometries of B···HX and the weakness of the intermolecular interaction when considered together provide the basis for scales of limiting, gas-phase nucleophilicity and electrophilicity. For a dimer of a given geometry, the strength of the interaction will then depend on the magnitude of the nucleophilicity of the site on B and the electrophilicity of HX but nevertheless will usually be sufficiently small to be described by the electrostatic model involving essentially undistorted charge distributions in B and HX (see below).

One common measure of the strength of binding in dimers is the dissociation energy, but this is rarely available. Recently, it has been shown how realistic values of the quadratic force constant (k_σ) for stretching the weak bond in B···HX can be calculated from the centrifugal distortion constants D_J or Δ_J obtained experimentally.[5] Consequently, a large number of k_σ values are now in the literature.[4] We therefore collect in Table I this quantity[6–35] for the series B···HX where B = N_2, CO, PH_3, H_2S,

---

[†] University of Exeter.

[‡] University College London.

(1) Legon, A. C.; Millen D. J. *Chem. Rev.* **1986**, *86*, 635.

(2) Legon, A. C.; Millen, D. J. *Faraday Discuss. Chem. Soc.* **1982**, *73*, 71.

(3) Buckingham, A. D; Fowler, P. W. *Can. J. Chem.* **1985**, *63*, 2018.

(4) Legon, A. C.; Millen, D. J. *Acc. Chem. Res.*, in press.

(5) Millen, D. J. *Can. J. Chem.* **1985**, *63*, 1477.

Table I. Observed and Calculated Intermolecular Stretching Force Constants (k_σ, N m^{-1}) for Dimers B···HX

	HX					
B	HF	HCl	HCN	HBr	HC≡CH	HCF_3
N_2	5.5 (5.5)[b]	2.5 (2.8)[c]	2.3 (2.3)[d]	(2.3)	[e]	[e]
CO	8.5 (8.5)[f]	3.9 (4.2)[g]	3.3 (3.6)[h]	3.0 (3.6)[i]	(2.0)	[e]
PH_3	10.9 (11.0)[j]	5.9 (5.5)[k]	4.3 (4.7)[l]	5.0 (4.6)[m]	(2.6)	(2.1)
H_2S	12.0 (12.0)[n]	6.8 (6.0)[o]	4.7 (5.1)[p]	5.9 (5.0)[q]	(2.9)	(2.3)
HCN	18.2 (18.3)[r]	9.1 (9.1)[s]	8.1 (7.8)[t]	7.3 (7.7)[u]	(4.4)	3.5 (3.5)[v]
CH_3CN	20.1 (20.3)[w]	10.7 (10.1)[x]	9.8 (8.6)[y]	(8.5)	4.7 (4.9)[z]	(3.9)
H_2O	24.9 (25.0)[aa]	12.5 (12.5)[bb]	11.1 (10.6)[cc]	(10.5)	6.5 (6.0)[dd]	(4.8)
NH_3	(28.8)	(14.4)	12.2 (12.2)[ee]	(12.1)	7.0 (6.9)[ff]	(5.5)

[a] Observed k_σ values have been obtained, where appropriate, from centrifugal distortion constants in the following papers according to the relevant expression given in ref 5. Calculated values using N and E from Table II in eq 1 are given in parentheses. [b] Reference 6. [c] Reference 7. [d] Reference 8. [e] Predicted values of $k_\sigma < 2.0$ are considered too small to be reliable. [f] Reference 9. [g] Reference 10. [h] Reference 11. [i] Reference 12. [j] Reference 13. [k] Reference 14. [l] Reference 15. [m] Reference 16. [n] Reference 17. [o] Reference 18. [p] Reference 19. [q] Reference 20. [r] Reference 21. [s] Reference 22. [t] Reference 23. [u] Reference 24. [v] Reference 25. [w] Reference 26. [x] Reference 27. [y] Reference 28. [z] Reference 29. [aa] Reference 30. [bb] Reference 31. [cc] Reference 32. [dd] Reference 33. [ee] Reference 34. [ff] Reference 35.

Table II. Values of (a) Nucleophilicities (N) and (b) Electrophilicities (E) of B and HX[a]

				(a) Nucleophilicities, N			
N_2	CO	PH_3	H_2S	HCN	CH_3CN	H_2O	NH_3
2.2	3.4	4.4	4.8	7.3	8.1	10.0	11.5
H_2CO		$(CN)_2$	HCCCN	$(CH_3)_3P$	$(CH_3)_3CCN$	$(CH_3)_2O$	
3.5	5.4	5.7	6.5	6.9	9.0	11.2	
				(b) Electrophilicities, E			
HF	HCl	HCN	HBr	HC≡CH	HCF_3		
10.0	5.0	4.25	4.2	2.4	1.9		

[a] Values of N calculated from k_σ for B···HF by using eq 1 and E = 10.0 for HF except as indicated in the footnotes to Table III.

HCN, CH_3CN, H_2O, and NH_3 and where X = F, Cl, CN, Br, C≡CH, and CF_3. Thus, in a column of Table I, X is fixed but B varies, while in a row X varies and B is fixed. A glance indicates that there is a simple relationship along rows and down columns. It is clear that k_σ (B···HF)/k_σ (B···HCl) has an almost constant value of approximately 2 for all B, whereas k_σ(B···HF)/k_σ(B···HCN) and k_σ(B···HF)/k_σ(B···HBr) are each approximately another constant, independent of B. This observation suggests that a nucleophilicity (N) can be assigned to each B and an electrophilicity (E) to each HX. The strength of the hydrogen bond, as measured by k_σ, is then given by

$$k_\sigma = cNE \tag{1}$$

where c is a constant of proportionality. We next arbitrarily assign N = 10 for H_2O and E = 10 for HF, leading to c = 0.25 N m^{-1}. The next step is to use the k_σ of B···HF to establish the N values of all the other B's. Finally, the N's for the set of B are used with the observed k_σ values of columns 3, 4, 5, 6, and 7 to obtain E for HCl, HCN, HBr, HC≡CH, and HCF_3, respectively. The nucleophilicities and electrophilicities thereby evaluated are recorded in Table II. The k_σ's calculated from eq 1 using the E and N values of Table II are shown in parentheses in Table I for each B···HX. The agreement of predicted and experimental values is remarkably good in view of the simplicity of eq 1. Thus, 30 k_σ values are predicted by only 14 of N and E. We have also included in Table II some values of N and E derived on the basis of a single k_σ value. In these cases, the k_σ's were determined either from centrifugal distortion constants (as above)[36-40] or from values of the hydrogen-bond stretching frequency (ν_σ) from infrared

---

(6) Soper, P. D.; Legon, A. C.; Read, W. G.; Flygare, W. H. *J. Chem. Phys.* **1982**, *76*, 292.

(7) Altman, R. S.; Marshall, M. D.; Klemperer, W. *J. Chem. Phys.* **1983**, *79*, 57.

(8) Goodwin, E. J.; Legon, A. C. *J. Chem. Phys.* **1985**, *82*, 4434.

(9) Legon, A. C.; Soper, P. D.; Keenan, M. R.; Minton, T. K.; Balle, T. J.; Flygare, W. H. *J. Chem. Phys.* **1980**, *73*, 583.

(10) Soper, P. D.; Legon, A. C.; Flygare, W. H. *J. Chem. Phys.* **1981**, *74*, 2138.

(11) Goodwin, E. J.; Legon, A. C. *Chem. Phys.* **1984**, *87*, 81.

(12) Keenan, M. R.; Minton, T. K.; Legon, A. C.; Balle, T. J.; Flygare, W. H. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 5583.

(13) Legon, A. C.; Willoughby, L. C. *Chem. Phys.* **1983**, *74*, 127.

(14) Legon, A. C.; Willoughby, L. C., unpublished results.

(15) Legon, A. C.; Willoughby, L. C. *Chem. Phys.* **1984**, *85*, 443.

(16) Willoughby, L. C.; Legon, A. C. *J. Phys. Chem.* **1983**, *87*, 2085.

(17) Willoughby, L. C.; Fillery-Travis, A. J.; Legon, A. C. *J. Chem. Phys.* **1984**, *81*, 20.

(18) Goodwin, E. J.; Legon, A. C. *J. Chem. Soc., Faraday Trans. 2* **1984**, *80*, 51.

(19) Goodwin, E. J.; Legon, A. C. *J. Chem. Soc., Faraday Trans. 2* **1984**, *80*, 1669.

(20) Jaman, A. I.; Legon, A. C. *J. Mol. Struct.* **1986**, *145*, 261.

(21) Legon, A. C.; Millen, D. J.; Willoughby, L. C. *Proc. R. Soc. London, Ser. A* **1985**, *401*, 327.

(22) Legon, A. C.; Campbell, E. J.; Flygare, W. H. *J. Chem. Phys.* **1982**, *76*, 2267.

(23) Campbell, E. J.; Buxton, L. W.; Flygare, W. H. *Chem. Phys.* **1982**, *56*, 399.

(24) Campbell, E. J.; Legon, A. C.; Flygare, W. H. *J. Chem. Phys.* **1983**, *78*, 3494.

(25) Goodwin, E. J.; Legon, A. C. *J. Chem. Phys.* **1986**, *84*, 1988.

(26) Cope, P.; Legon, A. C.; Millen, D. J.; Willoughby, L. C. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 1189.

(27) Legon, A. C.; Millen, D. J.; North, H. M., unpublished results.

(28) Howard, N. W.; Legon, A. C. *J. Chem. Soc., Faraday Trans. 2*, in press.

(29) Howard, N. W.; Legon, A. C. *J. Chem. Phys.*, in press.

(30) Cazzoli, G.; Favero, P. G.; Lister, D. G.; Legon, A. C.; Millen, D. J.; Kisiel, Z. *Chem. Phys. Lett.* **1985**, *117*, 543.

(31) Legon, A. C.; Willoughby, L. C. *Chem. Phys. Lett.* **1983**, *95*, 449.

(32) Fillery-Travis, A. J.; Legon, A. C.; Willoughby, L. C. *Proc. R. Soc. London, Ser. A* **1984**, *396*, 405.

(33) Petersen, K. I.; Klemperer, W. *J. Chem. Phys.* **1984**, *81*, 3842.

(34) Fraser, G. T.; Leopold, K. R.; Nelson, D. D., Jr.; Tung, A.; Klemperer, W. *J. Chem. Phys.* **1984**, *80*, 3073.

(35) Fraser, G. T.; Leopold, K. R.; Klemperer, W. *J. Chem. Phys.* **1984**, *80*, 1423.

(36) Baiocchi, F. A.; Klemperer, W. *J. Chem. Phys.* **1983**, *78*, 3509.

(37) Shea, J. A.; Kukolich, S. G. *J. Chem. Phys.* **1983**, *78*, 3545.

(38) Legon, A. C.; Soper, P. D.; Flygare, W. H. *J. Chem. Phys.* **1981**, *74*, 4936.

(39) Georgiou, K.; Legon, A. C.; Millen, D. J.; North, H. M.; Willoughby, L. C. *Proc. R. Soc. London, Ser. A* **1984**, *394*, 87.

(40) Hirani, H. L.; Legon, A. C.; Millen, D. J.; Willoughby, L. C. *J. Mol. Struct.* **1984**, *125*, 171.

Table III. Predicted Values of k_σ (N m^{-1}) for Some Series of Dimers That Have Been Incompletely Investigated[a]

B	HX					
	HF	HCl	HCN	HBr	HC≡CH	HCF_3
H_2CO	8.8[b]	4.4	3.7	3.7	2.1	
	13.5	6.7[c]	5.7	5.7	3.2	2.6
$(CN)_2$	14.3[d]	7.1	6.1	6.0	3.4	2.7
HCCCN	16.3[e]	8.1	6.9	6.8	3.9	3.1
$(CH_3)_3P$	17.3	8.6	7.3[f]	7.2	4.1	3.3
$(CH_3)_3CCN$	22.5[g]	11.3	9.6	9.5	5.4	4.3
$(CH_3)_2O$	28.1[h]	14.1	11.9	11.8	6.7	5.3

[a] An experimental k_σ is available for only one dimer in each series. This has been used in conjunction with the appropriate value of E from Table II to give an N value for B (also recorded in Table II). The N was then used to generate the remaining k_σ in the given row. The experimental k_σ was determined either from the appropriate centrifugal distortion constant (CD) or from ν_σ obtained from infrared spectroscopy (IR) via $\nu_\sigma = (2\pi)^{-1}(k_\sigma/\mu)^{1/2}$. The source of the experimental k_σ is referred to in the indicated footnote and its nature denoted by either CD or IR. The value for $H_2CO\cdots HCF_3$ is predicted as <2 and is omitted (see footnote *e* of Table I). [b] Reference 36(CD). [c] Reference 37(CD). [d] Reference 38(CD). [e] Reference 39(CD). [f] Reference 40(CD). [g] Reference 41(IR). [h] Reference 42(IR).

spectroscopy[41,42] by using the relationship $\nu_\sigma = (2\pi)^{-1}(k_\sigma/\mu)^{1/2}$.

III. Electrostatic Background to the Model

The nonbonding electron pair model receives strong support from quantum-mechanical calculations. When the total binding energy for hydrogen-bonded dimers is partitioned into polarization, charge transfer, exchange repulsion, and electrostatic contributions, it is found that the last is the dominant term.[43-46] In fact, it is sugggested that for many dimers the first three factors roughly cancel, leaving the total interaction energies closely parallel to the electrostatic terms.[43-46] Evidently, it is therefore possible as a first approximation for the strengths of hydrogen bonds to be modeled by electrostatics alone. Furthermore, Umeyama and Morokuma[43] have pointed out that the electrostatic contribution appears to be controlled mainly by the local interaction between the net charges on the proton acceptor atom and the net charge on the hydrogen-bonding proton, that is, in the present language, between the nucleophilic and electrophilic sites. We emphasize again that the electrostatic contribution refers to essentially unperturbed electron distributions. Thus, the representation of the binding energy in terms of E and N involves quantities which apply to molecules that are very nearly in the limit of weak perturbation, in contrast to gas-phase proton affinities which correspond to the other limit where the nucleophilic molecule is chemically modified by accepting the proton.

The above discussion is based on the dissociation energy (D_e) as a measure of the strength of binding. The scale of N and E values introduced here is based on the other measure of binding strength, namely, k_σ which measures the restoring force per unit infinitesimal displacement of the hydrogen bond. The success of the simple eq 1 apparently indicates that the electrostatic interpretation is applicable to k_σ as well as to D_e.

IV. Discussion

We have established, with the aid of the hydrogen-bond stretching force constants (k_σ), limiting, gas-phase nucleophilicities (N) and electrophilicities (E) for a number of molecules that serve as components B and HX in forming hydrogen-bonded dimers (see Table II). We note from Table II that E drops rapidly from HF to HCl and then more slowly from HCl to HCN and HBr. We also note that acetylene is more electrophilic than fluoroform. The order of nucleophilicities is $NH_3 > H_2O > CH_3CN > HCN > H_2S > PH_3 > CO > N_2$.

The E and N values of Table II can be used to predict k_σ values for dimers that have yet to be investigated experimentally. A selection of such predicted quantities is given in Tables I and III. We note in Table I that k_σ for the linear dimer HCN···HC≡CH falls, as expected, below the value of k_σ = 5.15 N m^{-1} for the observed (and presumably more stable) T-shaped dimer in which B is HC≡CH and X is CN.[47]

The quantities E and N introduced here should be of general interest and have some specific applications in the spectroscopy of dimers. For example, they can be used, as in Table III, to predict k_σ for an unknown B···HX and thence D_J or Δ_J prior to an investigation of its rotational spectrum. In addition, k_σ can be used to obtain $\nu_\sigma = (2\pi)^{-1}(k_\sigma/\mu)^{1/2}$ for the prediction of far-infrared spectra (fundamental of ν_σ) or near-infrared spectra (combination bands) of B···HX. This will be useful both in gas-phase and matrix-isolation work.

The long-term aim of our investigations of hydrogen-bonded dimers is to find methods for predicting the properties of the dimers from the known properties of the free components. We have previously shown how this can be done for hydrogen-bond directions by using simple rules.[2] In the present article, we have established a method of so predicting the strengths of hydrogen-bonded dimers (as measured by k_σ). Hence, two of the most important properties of dimers can now be readily, reliably, and widely predicted.

Registry No. N_2, 7727-37-9; CO, 630-08-0; PH_3, 7803-51-2; H_2S, 7783-06-4; HCN, 74-90-8; CH_3CN, 75-05-8; H_2O, 7732-18-5; NH_3, 7664-41-7; HF, 7664-39-3; HCl, 7647-01-0; HCN, 74-90-8; HBr, 10035-10-6; HC≡CH, 74-86-2; CF_3, 75-46-7.

---

(41) Georgiou, A. S.; Legon, A. C.; Millen, D. J. *Proc. R. Soc. London, Ser. A* **1980**, *370*, 257.

(42) Thomas, R. K. *Proc. R. Soc. London, Ser. A* **1971**, *322*, 137.

(43) Umeyama, H.; Morokuma, K. *J. Am. Chem. Soc.* **1977**, *99*, 1316.

(44) Hurst, G. J. B.; Fowler, P. W.; Stone, A. J.; Buckingham, A. D. *Int. J. Quantum Chem.* **1986**, *29*, 1223.

(45) Rendell, A. P. L.; Bacskay, G. B.; Hush, N. S. *Chem. Phys. Lett.* **1985**, *117*, 400.

(46) Buckingham, A. D.; Fowler, P. W.; Stone, A. J. *Int. Rev. Phys. Chem.* **1986**, *5*, 107.

(47) Aldrich, P. D.; Kukolich, S. G.; Campbell, E. J. *J. Chem. Phys.* **1983**, *78*, 3521.