

## A Thermodynamic Hydrogen-bond Acidity Scale for Monosubstituted Acetylenes

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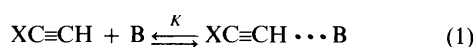
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A scale of solute hydrogen-bond acidity has been derived from measured equilibrium constants (as log  $K$  values) for hydrogen-bond complexation of a series of monosubstituted acetylenes against the reference base triphenylphosphine oxide in dilute  $\text{CCl}_4$  solution at 20 °C. The effects of the substituents Pent,  $\text{SiEt}_3$ ,  $\text{OEt}$ ,  $\text{Ph}$ ,  $\text{SnPh}_3$ ,  $\text{SEt}$ ,  $p\text{-BrC}_6\text{H}_4$ ,  $\text{ClCH}_2$ ,  $p\text{-NO}_2\text{C}_6\text{H}_4$ ,  $\text{COMe}$ ,  $\text{COOEt}$ ,  $\text{CF}_3$  and  $\text{CN}$  on the complexation reaction are discussed in terms of their field and resonance substituent constants. The relation between log  $K$  and the charge on the acetylenic proton indicates that electrostatic interaction predominates for these weak hydrogen-bond donors. Hydrogen-bond acidity is closely related to kinetic acidity. The log  $K$  values may be transformed into  $\alpha_2^{\text{H}}$  values suitable for use in linear solvation energy relationships.

It has long been known that monosubstituted acetylenes are weakly acidic.<sup>1</sup> Their Brønsted acidities can be measured from positions of proton transfer equilibrium ('equilibrium Brønsted acidity') either in solution, or in the gas phase, or alternatively can be calculated from the differences in molecular energy of the neutral acetylenes and the corresponding anions.<sup>1</sup> The rates of proton transfer are often easier to obtain than equilibrium constants, and provide 'kinetic acidity', but correlation with equilibrium acidity is not straightforward.<sup>1</sup>

The equilibrium constant of the hydrogen-bond complexation reaction of monosubstituted acetylenes with a reference base  $\text{B}$  in an inert solvent, eqn. (1), provides another measure



of acidity, the so-called 'hydrogen-bond acidity'.<sup>2,3</sup> Numerous processes such as solvent effects on rate or equilibrium constants, partition coefficients, solubilities, HPLC capacity factors and GLC retention indexes can be rationalized in terms of hydrogen-bond acidity and basicity.<sup>4</sup> Scales of solute hydrogen-bond acidity and basicity have been statistically constructed<sup>2,5</sup> using equilibrium constants (as log  $K$  values) for complexation of series of acids against a given base and series of bases against a given acid. The log  $K$  values may be transformed<sup>2,5</sup> into  $\alpha_2^{\text{H}}$  (hydrogen-bond acidity scale) and  $\beta_2^{\text{H}}$  (hydrogen-bond basicity scale) values suitable for use in linear solvation energy relationships.<sup>6</sup> The  $\beta_2^{\text{H}}$  and  $\alpha_2^{\text{H}}$  values also permit a quantitative estimate of the value of the formation constant for the hydrogen-bonded complex between any hydrogen-bond donor of known  $\alpha_2^{\text{H}}$  value and any hydrogen-bond acceptor of known  $\beta_2^{\text{H}}$  value [eqn. (2)].<sup>7</sup> Only limited combinations of acids and bases are excluded from the general equation (2).

$$\log K = 7.354 \alpha_2^{\text{H}} \beta_2^{\text{H}} - 1.094 \quad (2)$$

Because the weakly acidic monosubstituted acetylenes have, unfortunately, generally been complexed with weak bases (hence the equilibrium constants are very low and rather inaccurate), and because literature data are scarce, the statistical hydrogen-bond acidity scale<sup>2</sup> for monosubstituted acetylenes is of uncertain reliability and needs to be completed.

The purpose of the present work is to establish a reliable scale

of solute hydrogen-bond acidity for monosubstituted acetylenes with substituents spanning a wide range of reactivity. The scale is based on log  $K$  values for hydrogen-bond complexation of  $\text{XC}\equiv\text{CH}$  compounds given in Table 1 in  $\text{CCl}_4$  at 293 K, with the reference base triphenylphosphine oxide chosen because it is among the strongest known hydrogen-bond acceptors and obeys eqn. (2).

### Experimental

**Materials.**—Spectroscopic grade  $\text{CCl}_4$  was dried over 4 Å molecular sieves.  $\text{Ph}_3\text{PO}$  was recrystallized from absolute ethanol and dried *in vacuo*. In Table 1, alkynes **1**, **3**, **4**, **8**, **9**, **11**, **12** and **13** were commercial compounds. Alkynes **2**, **6**, **7**, **10** and **14** were prepared in our laboratory by known methods.<sup>8</sup> We gratefully acknowledge Pr. Cadiot for the gift of a sample of  $\text{Ph}_3\text{SnC}\equiv\text{CH}$ .

**Infrared Measurements.**—These were carried out with a Beckman IR 12 spectrometer, and checked with a Bruker IFS 45 Fourier transform spectrometer. The temperature of the quartz cell was maintained at  $20 \pm 0.5$  °C. The 1 cm path length permitted us to keep the alkyne concentration under the limit of self-association. The solutions were prepared and the cell was filled inside a dry box.

**Equilibrium Constants.**—They are defined by  $K = C_c/C_a \cdot C_b$ , where  $C_c$ ,  $C_a$  and  $C_b$  are, respectively, the equilibrium molar concentration of the complex, acid (acetylenes), and base ( $\text{Ph}_3\text{PO}$ ).  $C_c$  is determined from the absorbance of the free  $\nu(\equiv\text{CH})$  band. The equilibrium constant is taken as the mean of three values obtained from three  $\text{Ph}_3\text{PO}$  concentrations.  $K$  is estimated to be accurate to within 5–10%, hence log  $K$  is at  $\pm 0.02$  to  $\pm 0.05$  units.

### Results

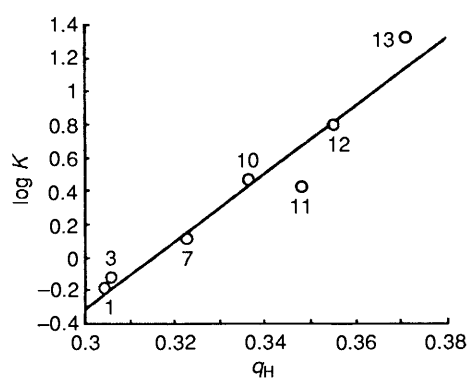
Values for log  $K$  for 14 acetylenes are reported in Table 1 which also contains (i) the wavenumber of the  $\nu(\equiv\text{CH})$  vibration, (ii) its molar extinction coefficient, and (iii)  $\Delta\nu(\equiv\text{CH})$ , the infrared wavenumber shift caused by hydrogen bonding with  $\text{Ph}_3\text{PO}$ .

$\Delta\nu(\equiv\text{CH})$  can be considered as a spectroscopic scale of hydrogen-bond acidity. It is excellently correlated with log  $K$

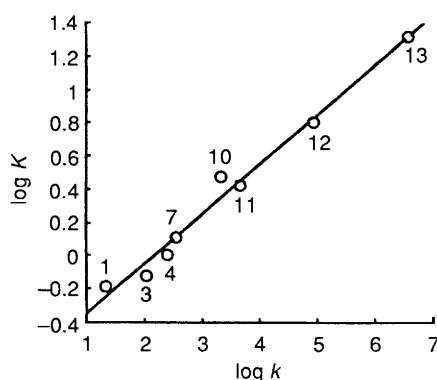
**Table 1** Infrared spectroscopic data and equilibrium constants for hydrogen-bond formation of monosubstituted acetylenes  $\text{XC}\equiv\text{CH}$  with triphenylphosphine oxide

No.	Substituent X	$\nu(\equiv\text{CH})^a$	$\Delta\nu(\equiv\text{CH})^b$	$\log K^c$	$\alpha_2^{d,e}$
1	Pent	3314 (205)	118	-0.19	0.13
2	$\text{Et}_3\text{Si}$	3293 (157)	128	-0.11	0.15
3	EtO	3333 (140)	133	-0.12	0.14
4	Ph	3314 <sup>d</sup> (145)	145	0	0.16
5	$\text{Ph}_3\text{Sn}$	3285 (170)	135	0.06	0.17
6	EtS	3313 (274)	149	0.15	0.18
7	<i>p</i> - $\text{BrC}_6\text{H}_4$	3313 <sup>d</sup> (183)	153	0.18	0.19
8	$\text{ClCH}_2$	3315 (221)	150	0.11	0.18
9	$\text{BrCH}_2$	3313 (215)	148	0.10	0.18
10	<i>p</i> - $\text{NO}_2\text{C}_6\text{H}_4$	3309 <sup>d</sup> (180)	169	0.21	0.19
11	COMe	3307 (166)	188	0.47	0.23
12	COOEt	3308 (250)	188	0.42	0.22
13	$\text{CF}_3$	3309 (e)	216	(0.81) <sup>f</sup>	0.28
14	CN	3303 (330)	258	1.32	0.36

<sup>a</sup>  $\text{cm}^{-1}$ . The molar extinction coefficient in  $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$  is given in parentheses. <sup>b</sup>  $\Delta\nu(\equiv\text{CH}) = \nu(\equiv\text{CH} \text{ free}) - \nu(\equiv\text{CH} \text{ hydrogen-bonded}) \text{ cm}^{-1}$ . <sup>c</sup> In  $\text{CCl}_4$  at 293 K. <sup>d</sup> Corrected for Fermi resonance. <sup>e</sup> Gaseous sample. <sup>f</sup> Calculated from the  $\log K/\Delta\nu(\equiv\text{CH})$  relationship [eqn. (3)]. <sup>g</sup>  $\alpha_2^{\text{H}} = (\log K + 1.094)/7.354 \times 0.919$ .



**Fig. 1** Relationship between the hydrogen-bond acidity of monosubstituted acetylenes and the net atomic charge of the terminal acetylenic hydrogen. Numbers refer to Table 1.



**Fig. 2** Relationship between the equilibrium hydrogen-bond acidity of monosubstituted acetylenes and the tritium isotope exchange rates ( $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ ). Numbers refer to Table 1.

[eqn. (3)]. The correlation coefficient  $r$  is 0.987 for 13 data and the standard deviation  $s = 0.06$  is of the order of experimental uncertainties.

$$\log K = 0.015 \Delta\nu(\equiv\text{CH}) - 1.46 \quad (3)$$

This excellent correlation between the thermodynamic ( $\log K$ ) and spectroscopic ( $\Delta\nu$ ) scales of hydrogen-bond acidity supports our thermodynamic results. It also allows the calcul-

ation of  $\log K$  for the gaseous  $\text{CF}_3\text{C}\equiv\text{CH}$  compound ( $\log K_{\text{calc}} = 0.81$ ).

## Discussion

**Substituents Effects.**—The hydrogen-bond acidity scale ranges from  $\log K = -0.19$  for hept-1-yne to  $\log K = 1.31$  for cyanoacetylene, by far the most acidic acetylene. The scale covers 9  $\text{kJ mol}^{-1}$  in Gibbs energy. The substituent effect seems mainly to be a field/inductive effect since the  $\sigma_{\text{F}}$  substituent constant<sup>9</sup> for field/inductive effects explains 83% of the variance of  $\log K$  ( $r^2$  is 0.83 for the correlation of  $\log K$  with  $\sigma_{\text{F}}$ ). This confirms previous findings.<sup>2</sup> However, in the regression of  $\log K$  with  $\sigma_{\text{F}}$ , the deviations of the  $\text{C}\equiv\text{N}$ ,  $\text{COOEt}$ ,  $\text{COMe}$  and  $\text{Et}_3\text{Si}$  substituents upwards of the 'inductive' regression line suggest an additional resonance electron-withdrawing effect for these groups, whereas the large downward deviations of the  $\text{OEt}$  and  $\text{SEt}$  groups is in accord with an additional resonance electron-donating effect of these substituents. We have therefore attempted the dual substituent parameter eqn. (4) where  $\sigma_{\text{R}}$  is the substituent resonance constant,  $\rho_{\text{F}}$  and  $\rho_{\text{R}}$  are the sensitivity coefficients of  $\log K$  to field/inductive and resonance effects, and  $\log K^\circ$  represents the parent compound  $\text{HC}\equiv\text{CH}$ .

$$\log K = \log K^\circ + \rho_{\text{F}} \sigma_{\text{F}} + \rho_{\text{R}} \sigma_{\text{R}} \quad (4)$$

It is not clear to us what kind of electron demand is exerted by the reaction centre in eqn. (1). The  $\sigma_{\text{R}}^+$  constant for  $\pi$ -electron deficient reaction centre and the  $\sigma_{\text{R}}^-$  constant for electron-rich reaction centre give equivalent multiple correlation coefficients ( $R = 0.977$  and  $0.979$ , respectively, for the nine substituents  $\text{Pent}$ ,  $\text{SiMe}_3$ ,  $\text{OEt}$ ,  $\text{Ph}$ ,  $\text{ClCH}_2$ ,  $\text{COMe}$ ,  $\text{COOMe}$ ,  $\text{CF}_3$  and  $\text{CN}$  for which  $\sigma_{\text{F}}$ ,  $\sigma_{\text{R}}^+$  and  $\sigma_{\text{R}}^-$  are given in reference 9). An adequate description of the data of Table 1 could be achieved by more sophisticated multiparametric extensions of the Hammett equation,<sup>10</sup> but we lack sufficient data for a statistically significant use of these extensions. The important result here is that resonance effects explain a significant supplementary part of the variance of  $\log K$  ( $R^2$  becomes 0.96 for the multiple correlation of  $\log K$  with  $\sigma_{\text{F}}$  and  $\sigma_{\text{R}}^+$  or  $\sigma_{\text{R}}^-$ ).

**The Nature of the Hydrogen Bond.**—Hydrogen-bond acidity of monosubstituted acetylenes can be related to the net atomic charge of the terminal acetylenic hydrogen computed by 4-31G calculations at the STO-3G geometries.<sup>11</sup> In this comparison substituents  $\text{COOEt}$ ,  $\text{CH}_2\text{Cl}$ ,  $\text{OEt}$  and  $\text{Pent}$  were represented, respectively, by the smaller substituents  $\text{COOMe}$ ,  $\text{CH}_2\text{F}$ ,  $\text{OMe}$  and  $\text{Et}$ . The differences introduced by this approximation are expected to be negligible. From Fig. 1 and eqn. (5) the hydrogen-bond acidity can be seen to increase regularly with the atomic charge  $q_{\text{H}}$ .

$$\log K = 20.5 q_{\text{H}} - 6.47 \quad (5)$$

$$r = 0.969 \quad n = 7 \quad s = 0.14$$

The classical electrostatic interaction between the  $\text{O}^{\delta-}$  and  $\text{H}^{\delta+}$  atoms is clearly predominant in the weak hydrogen bond between monosubstituted acetylenes and  $\text{Ph}_3\text{PO}$ .

**Comparison with Kinetic Acidity.**—Fig. 2 and eqn. (6) show the comparison of hydrogen-bond acidity in  $\text{CCl}_4$  with the hydroxide-catalysed rate constants for tritium isotope exchange in aqueous solution.<sup>11</sup>

$$\log K = 0.298 \log k - 0.65 \quad (6)$$

$$r = 0.992 \quad n = 8 \quad s = 0.07$$

The kinetic rates cover five orders of magnitude in reactivity. However it is clear that for the family of monosubstituted acetylenes, the energetics of hydrogen-bond formation is closely related to kinetic acidity, in spite of the fact that the first quantity refers to proton sharing in an inert solvent, while the second refers to full proton transfer in water. In particular this indicates that the acetylene anion solvation effects are relatively uniform throughout this series of monosubstituted acetylenes.

*The  $\alpha_2^H$  Scale.*—Since  $\beta_2^H$  for  $\text{Ph}_3\text{PO}$  is known to be 0.919, eqn. (2) allows the calculation of  $\alpha_2^H$  for monosubstituted acetylenes. They are reported in Table 1. We suggest that these homogeneous values based on a reference process might be preferred to the statistical values of reference 2.

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Paper 2/03651G

Received 9th July 1992

Accepted 18th September 1992