Acidities of Carbon Acids

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1 Introduction

Over the last fifty years or so physical chemists have concerned themselves with the development of precise methods of measuring acidity constants; these include conductance, electrometric, optical, and magnetic measurements which under favourable circumstances allow values to be quoted with a precision of $\pm 0{\cdot}001$ in pK_a. A number of standard works[1] deal with these methods in some detail and values of the dissociation constants of organic acids in aqueous solution have also been compiled.[2] The data for well over a thousand compounds serve to illustrate two factors in particular; firstly that in the majority of compounds the hydrogen undergoing ionisation is attached to oxygen, with compounds in which the hydrogen undergoing ionisation is attached to nitrogen a poor second; secondly that more than 95% of the pK_a's have values between 2 and 12.

In general, carbon acids are much weaker than oxygen acids with the result that many of the classical methods of determining acidity constants are no longer applicable, *e.g.* the conductance method becomes unreliable when a long extrapolation to obtain λ_∞ is necessary. In addition, it is no longer always possible to refer the pK_a to purely aqueous conditions. Consequently, considerable ingenuity has been expended in devising new methods of determining acid strengths and, not surprisingly in view of the extremely weak acidities sometimes encountered, many of them lack the rigour associated with the classical methods.

The equilibrium

$$RH \rightleftharpoons R^- + H^+ \qquad (1)$$

measures the intrinsic acidity of an acid. However, it takes no account of the solvent and for those carbon acids whose acidities can still be measured in aqueous media the equation

$$RH + H_2O \rightleftharpoons R^- + H_3O^+ \qquad (2)$$

serves to define the thermodynamic acidity constant

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[1] H. S. Harned and B. B. Owen, 'The Physical Chemistry of Electrolytic Solutions', Reinhold, New York, 1958; R. A. Robinson and R. H. Stokes, 'Electrolyte Solutions', Butterworths, London, 1959; C. B. Monk, 'Electrolytic Dissociation', Academic Press, London, 1961; C. W. Davies, 'Ion Association', Butterworths, London, 1962; J. E. Prue, 'Ionic Equilibria', Pergamon Press, London, 1966.

[2] G. Kortum, W. Vogel, and K. Andrussow, 'Dissociation Constants of Organic Acids in Aqueous Solution', Butterworths, London, 1961.

$$K_a = a_{R^-}\, a_{H_3O^+}/a_{RH} = \frac{[R^-][H_3O^+]}{[RH]}\,\frac{f_{R^-}f_{H_3O^+}}{f_{RH}} \tag{3}$$

a_{H_2O} being assumed constant; a's are activities, f's activity coefficients on the molar concentration scale, and [ ] denote concentration. K_a can then be determined under conditions where the activity coefficient expression reduces to unity or can be calculated.

For still weaker acids it is necessary to employ more basic media. Acidity constants in different media can then be related by

$$K_a(H_2O) = K_a(S)\,[f_{R^-}f_{H_3O^+}/f_{RH}] \tag{4}$$

where the last term represents the activity coefficients of the particular species in solvent S relative to a standard state in water and can be equated to the free energy required to transfer one mole of the species from its standard state in water to its standard state in solvent S. Difference in solvent basicities as well as electrostatic and hydrogen-bonding effects are major factors in accounting for the changes.

2 Methods of Determining Acidities of Carbon Acids

A. Competitive.—The basis of the method, as shown by Conant and Wheland[3] and also McEwen,[4] is the preparation of the sodium or potassium salts of the carbon acids in ether and their reaction with other carbon acids so that the equilibrium constant for the reaction

$$RH + R^1M \rightleftharpoons RM + R^1H \tag{5}$$

can be measured and the relative pK_a's of a series of carbon acids calculated from equation 6. Nearly thirty years later Applequist and O'Brien[5] undertook

$$pK_a - pK_a^1 = \log_{10}([R^1M]/[R^1H]) - \log_{10}([RM]/[RH]) \tag{6}$$

research to see whether the halogen metal interchange reaction

$$RI + R^1M \rightleftharpoons RM + R^1I \tag{7}$$

could be used to obtain quantitative data in the region of very low acidities. A somewhat similar study by Salinger and Dessy[6] of carbanion stabilities was made via the exchange reactions of organomercury and organomagnesium compounds:—

$$RMg + R^1Hg \rightleftharpoons RHg + R^1Mg \tag{8}$$

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[3] J. B. Conant and G. W. Wheland, *J. Amer. Chem. Soc.*, 1932, **54**, 1912.

[4] W. K. McEwen, *J. Amer. Chem. Soc.*, 1936, **58**, 1124.

[5] D. E. Applequist and D. F. O'Brien, *J. Amer. Chem. Soc.*, 1963, **85**, 743.

[6] R. M. Salinger and R. E. Dessy, *Tetrahedron Letters*, 1963, **11**, 729.

More recently, Streitwieser and co-workers[7] reported on measurements in which lithium or caesium salts are prepared in cyclohexylamine. In all cases studied the hydrocarbons were more acidic than cyclohexylamine so that the equilibrium

$$RH + MNHC_6H_{11} \rightleftharpoons RM + C_6H_{11}NH_2 \qquad (9)$$

lies well over to the right. Hence, a mixture of two such hydrocarbons in cyclohexylamine when treated with an insufficient amount of either lithium or caesium cyclohexylamide produces the equilibrium described by equation 5.

A suspension of sodium amide in liquid ammonia has also been used[8] to determine relative acidities, with the difference that instead of the customary spectrophotometric method of determining acid and anion concentrations n.m.r. spectroscopy was employed. The technique is particularly well suited in this case as the high volatility of ammonia makes it necessary to work at low temperatures or study the solutions under pressure. The spectra also reveal that the anions are formed by simple proton loss rather than by base addition as is sometimes the case.

Competitive methods give the difference in acid strength and in order to obtain an absolute value the pK_a of one of the acids must be known. Although measurements frequently refer to media in which ion association is appreciable its contribution is usually neglected. Finally, the use of a particular solvent-base system means that only acids covering a pK range of something less than 10 units can be studied.

B. Electrometric.—The acidity constants of the more acidic carbon acids ($pK_a \sim 4$—10) may be determined by measuring the pH of solutions of the acids partially neutralised (20—80%) with carbonate-free sodium hydroxide. Pearson[9] determined pK_a values for ethyl nitroacetate, nitroacetone, and malononitrile in this way and Long[10] determined that of 2-acetylcyclohexanone. The latter work is interesting as the results give the gross dissociation constant of substrate (pK_G), the ketone being a mixture of enol and keto forms in the ratio 3:7. The ionisation constant (pK_E) of the enol form is nearly 0·4 units lower than the pK_G value.

In theory there is no reason why the classical method of obtaining acidity constants from potentiometric titration could not be extended to much weaker acids provided the electrode system could be made to function reversibly. Ritchie[11] has shown that the glass electrode in dimethyl sulphoxide does just this up to a pK_a of approximately 28 by titrating various acids with solutions of dimsylcaesium in dimethyl sulphoxide.

Electrochemical data may be used in a thermodynamic pseudo-cycle in order

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[7] A. Streitwieser, J. I. Brauman, J. H. Hammons, and A. H. Pudjaatmaka, *J. Amer. Chem. Soc.*, 1965, **87**, 384; A. Streitwieser, J. H. Hammons, E. Ciuffarin, and J. I. Brauman, *ibid.*, 1967, **89**, 59; A. Streitwieser, E. Ciuffarin, and J. H. Hammons, *ibid.*, 1967, **89**, 63.

[8] T. Birchall and W. L. Jolly, *J. Amer. Chem. Soc.*, 1966, **88**, 5439.

[9] R. G. Pearson and R. L. Dillon, *J. Amer. Chem. Soc.*, 1953, **75**, 2439.

[10] T. Riley and F. A. Long, *J. Amer. Chem. Soc.*, 1962, **84**, 522.

[11] C. D. Ritchie and R. E. Uschold, *J. Amer. Chem. Soc.*, 1967, **89**, 1721, 2752; 1968, **90**. 2821.

to determine acidity constants. The fundamental idea as described by Breslow[12] is that the thermodynamics of the conversion of a carbon acid to its anion can be determined via the sequence

$$\text{R–H} \overset{1}{\rightleftharpoons} \text{R–OH} \overset{2}{\rightleftharpoons} \text{R}^+ \overset{3}{\rightleftharpoons} \text{R}\cdot \overset{4}{\rightleftharpoons} \text{R}^{\overline{\cdot}} \qquad (10)$$

Only for step 1 are data not easily obtainable and Breslow assumes that the difference in heat of formation of a hydrocarbon and its related alcohol is constant, at least for closely similar compounds. For step 2 the commonly available thermodynamic parameter is the $\mathrm{p}K_{\mathrm{R}^+}$, whilst for steps 3 and 4 the half-wave potentials for successive addition of two electrons can be determined by a variety of methods of which cyclic voltammetry is particularly suitable for obtaining reversible potentials with very reactive species. To enable absolute $\mathrm{p}K_\mathrm{a}$ values to be determined that of triphenylmethane is taken to be 33, the value found by McEwen.[4] It would seem that the method has considerable potential for determining extremely weak acidities, as witness the fact that a value of 51 was obtained for triphenylcyclopropene which would have been difficult to obtain by other methods.

C. Optical.—A solution of potassium amide in liquid ammonia is a highly basic medium, such weak acids as xanthene and triphenylmethane reacting essentially completely[13] in it. For still weaker acids the ionisation can be described by

$$\text{RH} + \text{NH}_2^- \rightleftharpoons \text{R}^- + \text{NH}_3 \qquad (11)$$

the equilibrium constant K being given by

$$K = a_{\mathrm{R}^-} a_{\mathrm{NH_3}} / a_{\mathrm{RH}}\, a_{\mathrm{NH_2}^-} \qquad (12)$$

The position of equilibrium may be monitored by using the absorption band(s) characteristic of the conjugate base or the amide ion or both. Because of the low dielectric constant of the medium, ion association will be an important factor even in dilute solution. The equilibrium between ion pairs and free ions,

$$\text{K}^+\text{NH}_2^- \rightleftharpoons \text{K}^+ + \text{NH}_2^- \qquad (13)$$

has an equilibrium constant (K_d) given by

$$K_\mathrm{d} = a_{\mathrm{K}^+}\, a_{\mathrm{NH_2}^-} / a_{\mathrm{K^+NH_2^-}} \qquad (14)$$

The carbon acid reacts with potassium amide to give the potassium salt of the conjugate base which can exist either as an ion pair or as free ions,

$$\text{R}^-\text{K}^+ \rightleftharpoons \text{R}^- + \text{K}^+ \qquad (15)$$

with an equilibrium constant (K_d') given by

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[12] R. Breslow and W. Chu, *J. Amer. Chem. Soc.*, 1969, **90**, 2165; R. Breslow and K. Balasubramanian, *ibid.*, 1969, **90**, 5183.

[13] J. H. Takemoto and J. J. Lagowski, *J. Amer. Chem. Soc.*, 1969, **91**, 3785.

$$K_d = a_{R^-}\, a_{K^+}/a_{R^-K^+} \qquad (16)$$

If the experimental conditions are such that it is possible to assume that the activities of various species can be replaced by concentration terms, and that the activity of the solvent remains constant, then the concentrations can be expressed in terms of the absorbance of these species at a characteristic wavelength. As conductivity measurements allow K_d and K_d' to be calculated, the acidity constant can be determined. pK_a values of 27·1 and 28·6 for di(tolyl)-methane and di-(4-methoxyphenyl)methane respectively at −34·5 °C were obtained in this way.[13]

D. Kinetic.—Acidity constants can be determined from kinetic measurements if it is possible to measure the rate of ionisation and assume that the reverse step, that of ion recombination, is diffusion-controlled.[14] From the theory of diffusion-controlled reactions[15] it is possible to show that in the case of two uncharged molecules the value of the rate constant in water at 25 °C will be $0{\cdot}7 \times 10^{10}$ l mol^{-1} s^{-1} whereas for oppositely-charged univalent ions the value is less certain, being between 10^{10} and 10^{11} l mol^{-1} s^{-1}.

The acidity constant of dimethyl sulphoxide was obtained[16] from measurements of the rate of reaction between tritiated dimethyl sulphoxide and hydroxide ion in water ($k^{T}_{OH^-} = 10^{-8}$ l mol^{-1} s^{-1}). The rate under these conditions will be less than that for dimethyl sulphoxide and hydroxide ions by the amount of the isotope effect k_H/k_T which can be estimated as being between 5 and 10. If we assume that the rate of the reverse process is 10^{10} then the pK_a comes out at between 32 and 33.

For hydroxide-catalysed reactions in which the rate of recombination is no longer diffusion controlled it is frequently possible to study the rates of ionisation in the presence of other bases, as the use of tritium at tracer concentrations allows the rates of very slow reactions to be measured.[17]

E. Acidity Functions.[18,19]—In an aqueous solution of base the equilibrium given by equation 1 is set up. K_{RH}, the thermodynamic equilibrium constant is given by

$$K_{RH} = a_{H^+}\, a_{R^-}/a_{RH} \qquad (17)$$

so that by rearranging we get

$$\log_{10}([R^-]/[RH]) = \log_{10}K_{RH} - \log_{10}(f_{R^-}/f_{RH})\, a_{H^+} \qquad (18)$$

A similar equation can be set up for the slightly weaker but structurally similar acid R^1H so that if the acidity of RH can be determined in aqueous buffer

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[14] R. E. Weston and J. Bigeleisen, *J. Amer. Chem. Soc.*, 1955, **76**, 3074.
[15] P. Debye, *Trans. Electrochem. Soc.*, 1942, **82**, 265.
[16] R. Stewart and J. R. Jones, *J. Amer. Chem. Soc.*, 1967, **89**, 5069.
[17] A. J. Kresge and Y. Chiang, *J. Amer. Chem. Soc.*, 1961, **83**, 2877.
[18] C. H. Rochester, *Quart. Rev.*, 1966, **20**, 511.
[19] K. Bowden, *Chem. Rev.*, 1966, **66**, 119.

solutions that of R^1H can also be found provided the last term in equation 19 is zero.

$$\mathrm{p}K_{\mathrm{RH}} - \mathrm{p}K_{\mathrm{R^1H}} = \log_{10}([\mathrm{RH}]/[\mathrm{R^-}]) - \log_{10}([\mathrm{R^1H}]/[\mathrm{R^{1-}}]) + \log_{10}(f_{\mathrm{RH}}f_{\mathrm{R^{1-}}}/f_{\mathrm{R^1H}}f_{\mathrm{R^-}}) \qquad (19)$$

This approach has been used extensively by Stewart and co-workers[20] and has the advantage that the acidity constants so derived can be made to refer to the standard state in water.

F. Indirect.—In principle, any method which reflects the affinity of carbanions for electron-acceptors, as for example the association of carbanions with mercurous ions according to the equilibrium

$$2\mathrm{R^-} + \mathrm{Hg^{2+}} \rightleftharpoons \mathrm{R_2Hg} \qquad (20)$$

can be employed to characterise their stability. Reutov[21] proposed that the rate constant for the electrochemical reduction of symmetrical organomercury compounds,

$$\mathrm{R_2Hg} + 2e \rightarrow 2\mathrm{R^-} + \mathrm{Hg} \qquad (21)$$

depends on the affinity of R^- for Hg^{2+}, and on this basis suggested that for different carbon acids

$$\Delta(\alpha E_{\frac{1}{2}}) = \rho\Delta \mathrm{p}K_a, \qquad (22)$$

$E_{\frac{1}{2}}$ being the half-wave potential, α the transfer coefficient, and ρ a constant dependent on solvent. A good relationship between $\alpha E_{\frac{1}{2}}$ of R_2Hg and $\mathrm{p}K_a$ of RH was found, thereby making it possible to estimate $\mathrm{p}K_a$ values of other carbon acids.

For those carbon acids for which the rates of water-catalysed ionisation and acidity constants are known the data have been brought together by Pearson[9] and more recently by the author,[22] who finds that the relationship between $\log k$ and $\mathrm{p}K_a$ takes the form of a curve the slope of which increases with decreasing acid strength. With the exception of two cyano-compounds all others exhibit deviations of less than 1 pK unit in either direction from the curve drawn (see Figure).

Many carbon acids are aromatic hydrocarbons which form planar anions on ionisation and are therefore well suited to examination by molecular orbital theories.[23] For the reaction

$$\mathrm{RH} \rightarrow \mathrm{R^-} + \mathrm{H^+} \qquad (23)$$

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[20] R. Stewart and J. P. O'Donnell, *J. Amer. Chem. Soc.*, 1962, **84**, 493; K. Bowden and R. Stewart, *Tetrahedron*, 1965, **21**, 261; R. Stewart and D. Dolman, *Canad. J. Chem.*, 1967, **45**, 911.

[21] K. P. Butin, I. P. Beletskaya, A. N. Kashin, and O. A. Reutov, *J. Organometallic Chem.*, 1967, **10**, 197.

[22] J. R. Jones, *Progr. Phys. Org. Chem.*, (in press).

[23] H. Fischer and D. Rewicki, *Progr. Org. Chem.*, 1968, **7**, 116.

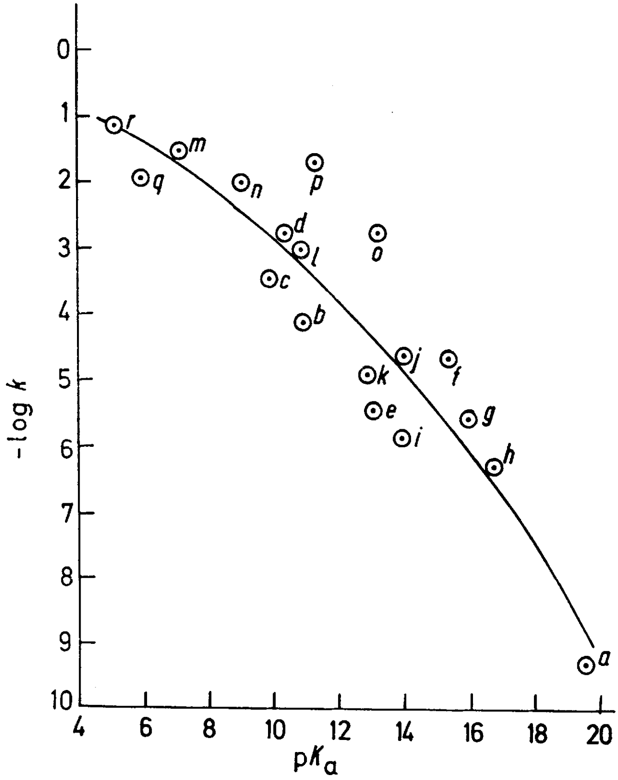

Figure *Plot of log* k *against* pK_a *for carbon acids in water at* 25°C. [a] acetone, R. P. Bell and O. M. Lidwell, *Proc. Roy. Soc.*, 1940, A, **88**, 176; R. P. Bell and P. W. Smith, *J. Chem. Soc.* (*B*), 1966, 241; R. P. Bell, G. R. Hillier, J. W. Mansfield, and D. G. Street, *ibid.*, 1967, 827; [b] methylacetylacetone, F. A. Long and D. Watson, *J. Chem. Soc.*, 1958, 2019; T. Riley and F. A. Long, *J. Amer. Chem. Soc.*, 1962, **84**, 522; [c] 2-acetylcyclohexanone, T. Riley and F. A. Long, *ibid.*, 1962, **84**, 522; [d] 2-carbethoxycyclopentanone, R. P. Bell, J. A. Fendley, and J. R. Hulett, *Proc. Roy. Soc.*, 1956, A, **235**, 453; [e] 2-carbethoxycyclohexanone, R. P. Bell and H. L. Goldsmith, *ibid.*, 1952, A, **210**, 322; R. P. Bell and E. Gelles, *ibid.*, 1952, A, **210**, 310; [f] ethyl malonate, R. P. Bell and J. E. Crooks, *ibid.*, 1965, A, **286**, 285; C. Vermesse-Jacquinot, R. Schaal, and P. Rumpf, *Bull. Soc. chim. France*, 1960, 2030; [g] sym-dichloroacetone, R. P. Bell and J. Hansson, *Proc. Roy. Soc.*, 1960, A, **255**, 214; R. P. Bell and E. Gelles, *ibid.*, 1952, A, **210**, 310; [h] ethyl pyruvate, R. P. Bell and H. F. F. Ridgewell, *ibid.*, 1967, A, **298**, 178; [i] potassium propane-2-one-1-sulphonate, R. P. Bell and G. A. Wright, *Trans. Faraday Soc.*, 1961, **57**, 1381; [j] potassium propane-2-one-1,3-disulphonate, R. P. Bell, G. R. Hillier, J. W. Mansfield, and D. G. Street, *J. Chem. Soc.* (*B*), 1967, 827, [k] ethyl 2-methylacetoacetate, R. P. Bell and J. E. Crooks, *Proc. Roy. Soc.*, 1965, A, **286**, 285; R. G. Pearson and R. L. Dillon, *J. Amer. Chem. Soc.*, 1953, **75**, 2439; [l] ethyl acetoacetate, refs. *k*; [m] bromoacetylacetone, refs. *k*; [n] acetylacetone, refs. *k*; [o] t-butylmalononitrile, F. Hibbert, F. A. Long, and E. A. Walters, *J. Amer. Chem. Soc.*, 1969, **91**, 2381; R. H. Boyd and C. H. Wang, *ibid.*, 1965, **87**, 430; [p] malononitrile, refs. *o*; [q] ethyl nitroacetate, R. P. Bell and T. Spencer, *Proc. Roy. Soc.*, 1959, A, **251**, 41; R. G. Pearson and R. L. Dillon, *J. Amer. Chem. Soc.*, 1953, **75**, 2439; [r] nitroacetone, R. P. Bell and R. R. Robinson, *Proc. Roy. Soc.*, 1962, A, **298**, 178; refs. *q*.

the π-bond energy of the acid is

$$E_{\pi} = n\alpha + M\beta \qquad (24)$$

where n is the number of π-electrons, M a dimensionless number obtained from the Hückel molecular orbital calculations, and β the bond integral. For the anion

$$E_{\pi}^{-} = (n + 2)\alpha + M^{-}\beta \qquad (25)$$

so that the change in π-bond energy on forming the anion is

$$E_{\pi} = 2\alpha + \Delta M\beta \qquad (26)$$

If, therefore, the increase in π-conjugation in the change from acid to anion is the most important factor in determining the acidities of hydrocarbons, a linear relationship between $\mathrm{p}K_a$ and ΔM would be expected and has in fact been found in practice.[23]

G. Miscellaneous—The method of Wheland[24] provides a precise spectrophotometric method for determining acidities provided there is a shift in absorption maximum on ionisation. Long[25] developed a method suitable for uncharged acids having $\mathrm{p}K_a$ values in the range 10—15 and a distribution method has been used to obtain the $\mathrm{p}K_a$ of fluoradene.[26]

The possibility of a direct relationship between the acidity and basicity of compounds has been considered[27] and a method has been developed[28] for determining the acidity of weak carbon acids based on the fact that n.m.r.

Table 1 *Acidities of Cyanocarbon Acids*

Acid	$\mathrm{p}K_a$*
Methyl cyanide	$\simeq 25^{a}$
1,4-Dicyano-2-butene	$20\text{—}21^{b}$
t-Butylmalononitrile	$13{\cdot}1^{c}$
Malononitrile	$11{\cdot}20^{d}$
Bromomalononitrile	$\simeq 5^{a}$
p-(Tricyanovinyl)phenyldicyanomethane	$0{\cdot}75^{d}$
Methyl dicyanoacetate	$-2{\cdot}8^{d}$
Hexacyanoheptatriene	$-3{\cdot}55,^{e}$ $-3{\cdot}90$†
Cyanoform	$-5{\cdot}13,^{e}$ $-5{\cdot}0$†
Tricyanovinylalcohol	$-5{\cdot}3,^{e}$ $-5{\cdot}0$†
Tetracyanopropene	$< -8^{e}$
Hexacyanoisobutylene	$< -8{\cdot}5^{e}$

* The reference solvent is water; † the two values refer to $HClO_4$ and H_2SO_4 media respectively; [a] quoted in ref. 9; [b] E. A. Walters and F. A. Long, *J. Amer. Chem. Soc.*, 1969, **91**, 3733; [c] F. Hibbert, F. A. Long, and E. A. Walters, *J. Amer. Chem. Soc.*, 1969, **91**, 2381; [d] R. H. Boyd and C. H. Wang, *J. Amer. Chem. Soc.*, 1965, **87**, 430; [e] R. H. Boyd, *J. Phys. Chem.*, 1963, **67**, 737.

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[24] R. S. Stearns and G. W. Wheland, *J. Amer. Chem. Soc.*, 1947, **69**, 2025.

[25] P. Ballinger and F. A. Long, *J. Amer. Chem. Soc.*, 1959, **81**, 1050.

[26] H. Rapoport and G. Smolinsky, *J. Amer. Chem. Soc.*, 1958, **80**, 2910.

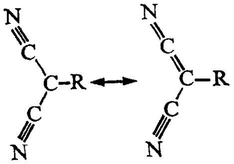
[27] E. M. Arnett, *Progr. Phys. Org. Chem.*, 1963, **1**, 223.

[28] D. J. Schaeffer, *Chem. Comm.*, 1970, 1043.

spectroscopy provides a measure of the electron density in the vicinity of a proton or group of protons.

3 Results and Discussion

The acidities of hydrocarbons are greatly influenced by the presence of adjacent activating groups of which cyano, sulphone, nitro, and carbonyl are amongst the most familiar. The effects of the first three only will be discussed in this article. In the case of cyanocarbon acids (Table 1) very simple structural modifications lead to an extremely wide range of acidities ($-10 < pK_a < 30$) which in some cases result in compounds which surpass mineral acids in strength. The cyanocarbons are remarkably stable to hydrolysis and the process of ionisation seems both uncomplicated and reversible. Their very strong acidities are due to resonance stabilisation in the anion,



(27)

which is not possible in the uncharged form.

The acidities of a number of sulphones (Table 2) are much higher than commonly supposed (from an extrapolation based on the relationship between rates of proton transfer and pK_a's of ketones Pearson[9] estimated a pK_a of 23 for dimethyl sulphone). Examination shows that whereas methyl substitution for hydrogen results in an increase of 1·5—2 pK_a units (compare $MeSO_2Ph$ with $MeCH_2SO_2Ph$) phenyl substitution causes a decrease of 6·5 pK_a units [compare Me_2SO_2 with $(PhCH_2)_2SO_2$]. The effect of methyl substitution in the

Table 2 *Acidities of Sulphones in Dimethyl Sulphoxide*[a]

Acid	pK_a*
Dimethyl sulphone	28·5
Methyl phenyl sulphone	27
Ethyl phenyl sulphone	29
Dibenzyl sulphone	22
Di-α-methylbenzyl sulphone	23·5
Trimethylene sulphone	> 30
Tetramethylene sulphone	> 31
Pentamethylene sulphone	> 31

* 4-Nitroaniline was used as the reference acid; [a] F. G. Bordwell, R. H. Imes, and E. C. Steiner, *J. Amer. Chem. Soc.*, 1967, **89**, 3905.

series nitromethane, nitroethane, and 2-nitropropane is, however, different (Table 3) as the acidity increases in the order given in contrast to the rates of reaction with hydroxide ion which decrease in the same sequence.[29] Clearly, methyl substitution retards proton abstraction by the nitronate ion from the solvent to a greater extent than it does the forward reaction. Further studies[30,31] on nitro-compounds in which steric factors are either absent or remain constant show that the rates of ionisation are more sensitive to the effects of a substituent than are the acidities. These findings have important implications concerning the widely adopted procedure of using Brønsted coefficients for measuring transition state structure.[30,32]

Table 3 *Acidities of Nitro-compounds*

Acid	pK_a*
Nitromethane	10·24,[a] 15·9[b]
Nitroethane	8·4[c], 13·9[b]
2-Nitropropane	7·7—7·8[a]
1-Nitropropane	8·98[a]
2-Nitrobutane	9·4[d]
1-Nitrobutane	10·0[d]
Nitrocyclobutane	9·26[e]
Nitrocyclopentane	7·91[e]
Nitrocyclohexane	8·92[e]
Nitrocycloheptane	7·65[e]
Nitrocyclo-octane	7·26[e]
Tris-(*p*-nitrophenyl)methane	13·8,[f] 12·2[b]
2,4′-Dinitrodiphenylmethane	17·38[g]
3,4′-Dinitrodiphenylmethane	17·62[g]
4,4′-Dinitrodiphenylmethane	15·85[g]
4,4′,4″-Trinitrotriphenylmethane	14·32[g]

* pK_a values in refs. *a* and *c* refer to H_2O, in ref. *b* to dimethyl sulphoxide, in ref. *d* to 50% (v/v) aqueous ethanol, in ref. *e* to 33% (w/w) methanol–water, and in ref. *g* to ethanolic dimethyl sulphoxide; [a] G. W. Wheland and J. Farr, *J. Amer. Chem. Soc.*, 1943, **65**, 1433; [b] ref. 11, p. 1721, 2821; [c] M. J. Gregory and T. C. Bruice, *J. Amer. Chem. Soc.*. 1967, **89**, 2327; [d] N. Kornblum, R. L. Blackwood, and J. W. Powers, *J. Amer. Chem. Soc*,, 1957, **79**, 2507; [e] P. W. Flanagan, H. W. Amburn, H. W. Stone, J. G. Traynham, and H. Shechter, *J. Amer. Chem. Soc.*, 1969, **91**, 2797; [f] quoted in ref. 11, p. 1721; [g] K. Bowden and R. Stewart, *Tetrahedron*, 1965, **21**, 261.

The effect of ring size on acidity can be seen in the case of the nitrocycloalkanes (Table 3) where the order 8 > 7 > 5 > 6 > 4 has been taken to imply that steric factors are important.[33] The difficulty of predicting acidity constants on

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[29] R. P. Bell and D. M. Goodall, *Proc. Roy. Soc.*, 1966, **A**, **273**, 294.

[30] F. G. Bordwell, W. J. Boyle jun., J. A. Hautala, and K. C. Lee, *J. Amer. Chem. Soc.*, 1969, **91**, 4002.

[31] M. Fukuyama, P. W. K. Flanagan, F. T. Williams, jun., L. Frainier, S. A. Miller, and H. Shechter, *J. Amer. Chem. Soc.*, 1970, **92**, 4689.

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[33] H. C. Brown and M. Bordowski, *J. Amer. Chem. Soc.*, 1952, **74**, 1952.

the basis of ring size is illustrated by the fact that 2-carbethoxycyclopentanone is both from a kinetic and equilibrium standpoint a stronger acid than the corresponding hexanone, whereas classical theory indicates that cyclohexene (unlike cyclopentene) can be formed without appreciable strain.[34]

The fact that tris-(*p*-nitrophenyl)methane is a stronger acid in dimethyl sulphoxide than is nitromethane (Table 3), whereas in aqueous solution the acidities are reversed, illustrates the dangers of comparing acidities in different solvents. The insufficient data on acidity constants in different media do not allow a detailed analysis, but it can be said that for those carbon acids which on ionisation form anions in which the charge density is concentrated on atoms more electronegative than carbon, interaction with the solvent may be considerable. In such cases, acidity constants in a given medium may not bear much relation to those in another.

The addition of extra activating groups increases the acidity although the magnitude of the effect falls with increasing numbers. Associated with this, at least for aromatic nitro-compounds, where a number of different species can result from reaction with the unshared electron pair of the base,[35] is the tendency for the ionisation process to become anomalous. Thus, 2-nitrofluorene, 2,5- and 2,7-dinitrofluorene, 3,3-dinitrodiphenylmethane, and 2,4,6-trinitrotoluene do not ionise normally in basic media.

The acidities of hydrocarbons have long been of interest, partly because they are frequently π-electron molecules for which there is a reasonably satisfactory theory. The majority of the pK_a's reported in Tables 4 and 5 were obtained by the acidity function approach, which had not been extensively used up to 1966 and which only recently has been criticised[11] on the grounds that (*a*) large deviations between the behaviour of 9-phenylfluorene and 4-nitroaniline in aqueous dimethyl sulphoxide are observed[36] and (*b*) the relative acidity of malonitrile and 9-carbomethoxyfluorene changes by 2·5 p*K* units in going from ethanol to dimethyl sulphoxide, whereas the relative acidities of 9-carbomethoxyfluorene and 9-phenylfluorene are nearly the same in both solutions.[11] In the first case the behaviour of 4-nitroaniline in highly basic media is now known to be very solvent dependent.[37] Secondly, the solvents referred to are entirely different, those used in setting up the H_- scale only differ in the proportion of dimethyl sulphoxide present.

Supporting evidence for the validity of the H_- scale comes from a number of studies. The basicity of ethanolic dimethyl sulphoxide containing base parallels that of methanolic dimethyl sulphoxide over a mole % dimethyl sulphoxide range from 0—90, although carbon acids were employed in the first system and nitrogen acids in the second.[20,38] H_- values for the first medium have recently been redetermined using nitrogen acids and differ little from those previously

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[34] R. P. Bell and H. L. Goldsmith, *Proc. Roy. Soc.*, 1952, A, **210**, 322.
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[36] E. C. Steiner and J. D. Starkey, *J. Amer. Chem. Soc.*, 1967, **89**, 2751.
[37] R. Stewart and J. P. O'Donnell, *Canad. J. Chem.*, 1964, **42**, 1511.
[38] R. Stewart, J. P. O'Donnell, D. J. Cram, and B. Rickborn, *Tetrahedron*, 1962, **18**, 917.

determined.[39] An H_- scale constructed in water–dimethyl sulphoxide mixtures containing base using a number of substituted fluorenes compares closely with that established using aniline indicators.[40] Indirect support comes from a kinetic study of the rates of tritium exchange of dimethyl sulphoxide in three different systems.[41] The results cover an H_- range of more than 8 units and are described by a single log k *vs.* H_- plot (slope +0·93). Finally, the acidity of 9-phenylfluorene in ethanol–dimethyl sulphoxide[20] (18·59), water–dimethyl sulphoxide[40] (18·59), and water–tetramethylene sulphone[42] (18·49) is virtually unchanged.

Where comparison is possible, the acidities of the fluorenes (Table 4) are very similar in dimethyl sulphoxide–ethanol and dimethyl sulphoxide–water mixtures but in dimethyl sulphoxide itself they are, on average, 2 pK units lower. Acidities in dimethyl sulphoxide are nearly 6 pK units lower than in methanol, probably

Table 4 *Acidities of Some Fluorenes in Different Media*

Acid			pK_a*		
	A	*B*	*C*	*D*	*E*
9-Cyanofluorene	11·41			8·4	14·2
9-Carbomethoxyfluorene	12·88			10·3	15·8
9-Phenylfluorene	18·59	18·59	18·1	16·4	
9-Methylfluorene		21·80		19·7	
4-Methoxyfluorene				20·0	
1-Methoxyfluorene				20·8	
2-Methoxyfluorene		22·36		21·1	
Fluorene	21·0	22·10	20·5	20·5	
2-Nitrofluorene		17·95			
2-Cyanofluorene		18·96			
2-Bromofluorene		20·56			
2-Chlorofluorene		20·59			
9-Ethylfluorene		22·22			
9-Isopropylfluorene		22·70			
9-t-Butylfluorene		23·41			

* *A*, Acidity function approach in dimethyl sulphoxide–ethanol with malononitrile, whose pK_a was measured in aqueous solution as the reference acid (K. Bowden and R. Stewart, *Tetrahedron*, 1965, **21**, 261); *B*, Acidity function approach in dimethyl sulphoxide–water with 9-phenylfluorene as the reference acid (K. Bowden and A. F. Cockerill, *J. Chem. Soc.* (*B*), 1970, 173); *C*, Acidity function approach in dimethyl sulphoxide–methanol with nitrogen acids as reference (E. C. Steiner and J. D. Starkey, *J. Amer. Chem. Soc.*, 1965, **87**, 382; E. C. Steiner and J. D. Starkey, *ibid.*, 1967, **89**, 2751); *D*, Potentiometric method in dimethyl sulphoxide (ref. 11; also C. D. Ritchie, *J. Amer. Chem. Soc.*, 1969, **91**, 6749); *E*, Electrometric method in which acid is partially neutralised (C. D. Ritchie, *J. Amer. Chem. Soc.*, 1969, **91**, 6749).

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[39] R. Stewart and A. Albagli, unpublished findings.

[40] K. Bowden and A. F. Cockerill, *J. Chem. Soc.* (*B*), 1970, 173.

[41] A. Albagli, J. R. Jones, and R. Stewart, *J. Chem. Soc.* (*B*), 1970, 1509.

[42] C. H. Langford and R. L. Burwell, *J. Amer. Chem. Soc.*, 1960, **82**, 1503.

because dispersion interactions with the highly polarisable solvent are more important than both dispersion and hydrogen-bonding stabilisation in methanol.[11] The effect of 2-substituents on the acidities of the fluorenes can be represented by a Hammett-type equation, the slope of which (approx. 7) is consistent with the considerable charge delocalisation experienced on ionisation.

Table 5 *Acidities of Some Hydrocarbons in Different Media*

Acid	pK_a*			
	A	*B*	*C*	*D*
9-Phenylfluorene	18·49	18·49	16·4	
7*H*-Benzo[*c*]fluorene	19·45	19·38		
Indene	19·93	20·24	18·5	
11*H*-Benzo[*a*]fluorene	20·05	19·97		
7*H*-Benz[*de*]anthracene	21·17	20·67		
4*H*-Cyclopenta[*def*]phenanthrene	22·63	22·60	20·0	
Fluorene	22·94	22·83	20·5	
11*H*-Benzo[*b*]fluorene	23·17	23·16		
1,1,3,3-Tetraphenylpropene		26·19		
1,1,3-Triphenylpropene	26·59	26·39		
10-Phenyl-9,9-dimethylanthracene	28·04			
9-Phenyl-9*H*-xanthene	28·5			25·8†
Biphenyl-4-yldiphenylmethane	30·2			
Triphenylmethane	31·48			28·8†
Diphenylmethane	33·1			30·2

* *A*, Competitive method using caesium cyclohexylamide in cyclohexylamine and 9-phenylfluorene as reference acid (A. Streitweiser, E. Ciuffarin, and J. H. Hammons, *J. Amer. Chem. Soc.*, 1967, **89**, 63); *B*, Competitive method using lithium cyclohexylamide in cyclohexylamine and 9-phenylfluorene as reference acid (A. Streitweiser, J. H. Hammons, E. Ciuffarin, and J. I. Brauman, *J. Amer. Chem. Soc.*, 1967, **89**, 59); *C*, Potentiometric method in dimethyl sulphoxide (ref. 11); *D*, Acidity function approach in dimethyl sulphoxide using 4-nitroaniline as reference acid (E. C. Steiner and J. M. Gilbert, *J. Amer. Chem. Soc.*, 1965, **85**, 383).

† The same values were obtained in water–dimethyl sulphoxide and methanol–dimethyl sulphoxide mixtures.

The 9-alkylfluorenes follow the order expected from inductive effects and correlate well with the Taft σ^* values.[43]

Relative acidities of hydrocarbons in lithium and caesium cyclohexylamides (Table 5) are very much the same, with the possible exception of indene which is substantially more acidic towards caesium cyclohexylamide than towards lithium cyclohexylamide. The surprisingly good agreement, in view of the extensive ion association that occurs in these media, has its counterpart in studies of oxygen and nitrogen acids.[44] Acidities determined in this way have a significance only with respect to the particular solvent employed.

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[43] K. Bowden, A. F. Cockerill, and J. R. Gilbert, *J. Chem. Soc. (B)*, 1970, 179.

[44] R. P. Bell, 'The Proton in Chemistry', Methuen, London, 1959, p. 58.

4 Conclusion

Although the available data on the acidities of carbon acids are not extensive, it is nevertheless clear that in a number of respects, *e.g.* the effects of substituents and ring size, the results are capable of interpretation in a similar manner to that adopted for the corresponding oxygen and nitrogen acids. Most of the acidities referred to have been obtained by the acidity function approach and the data presented provide clear evidence that the H_- function is, at least in certain media, independent of the acid used and that the scale is therefore a good deal more comprehensive than its H_0 counterpart. This is not entirely surprising as the H_0 scale refers to concentrated solutions of acid, whereas the H_- scale refers to a medium in which the concentration of base is being kept at a low and approximately constant value, the increased basicity arising mainly from an increase in the activity of the free base and a decrease in the activity of the solvent.

It is unfortunate that many of the acidities determined by the acidity function approach are related to that of 4-nitroaniline or another acid whose ionisation is highly solvent dependent. Although extrapolation techniques[45] have been developed to allow for medium effects, they do not provide any information concerning the ionisation process. Where uncertainty concerning the exact mode of ionisation exists there is a clear need to employ more than one analytical technique, *e.g.* n.m.r. spectroscopy can be used to supplement the information obtained from spectrophotometry and reveal whether radical anions and/or radicals may have been formed by electron transfer from carbanion to a neutral molecule. Thus, in the interaction of several nitrophenylmethanes with base, spectral shifts brought about by solvent changes are now known to be due mainly to the formation of such species.[46]

The behaviour of carbon acids in basic media differs greatly from that of oxygen and nitrogen acids in that, where comparison is possible, the rates of ionisation are much slower and cannot be explained on the basis of some peculiar property of the carbon–hydrogen bond. Where studies may be of benefit, *e.g.* activity coefficient behaviour in different solvents, and rate and acidity constant determinations in the same solvent, there are but few data available. Nevertheless, there are indications[47] that the rates of proton transfer reactions are much faster in non-hydroxylic solvents than would be expected on the basis of differences in basicity. Structural reorganisation accompanying the formation of the anion, and solvent reorganisation, which may involve the breakage of hydrogen bonds, both seem to be important factors that have to be considered.

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[46] C. A. Fyfe, A. Albagli, and R. Stewart, *Canad. J. Chem.*, 1970, **48**, 3721.

[47] C. D. Ritchie, *J. Amer. Chem. Soc.*, 1969, **91**, 6749.