Basicity Studies of a Series of 4,4-Dimethylcyclohexa-2,5-dienones

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Measurements have been made of the equilibrium protonation behaviour of a series of alkylcyclohexa-2,5-dienones. All follow the amide acidity function H_A quite closely, and their pK values can be correlated with those of related cyclohex-2-enones.

IN connection with our kinetic studies of dienone–phenol rearrangements[1] we needed to measure the equilibrium protonation behaviour of a number of alkylcyclohexadienones. This paper relates to the cyclohexa-2,5-dienones (1)—(5) whose rearrangements are reported in the following paper.[1a] Another dienone (6) which does not rearrange appreciably in acid is reported for comparison purposes.

The dienones (1)—(6), are weak bases and we used acidity function methods † to determine their basicities. The u.v. spectra of each dienone were recorded at known concentration in sulphuric or perchloric acids of known strength, and the absorbance at selected wavelengths used to find the pK. Because adherence to any one acidity function could not be assumed, data and calculation methods were used which would allow the most reliable tests of the correlation with established acidity functions. Three, well-separated wavelengths were used, close to the absorbance maximum of the free base, and the two maxima of the cation. The shorter wavelength cation peak was usually free of medium effects, but the other wavelengths show significant medium effects in the more concentrated acids. The calculated basicity parameters are weighted to reflect the lower reliability of values based on the latter wavelengths. The method of Katritzky, Waring, and Yates,[3] which uses the sigmoid curve of ε_λ against an arbitrarily chosen acidity function was used directly.‡

Contrary to comments in ref. 4, errors are easily estimated in this method and there is little difficulty in estimating the gradient of the inflection of the sigmoid curve at the half-protonation point. The curve is essentially straight in the half-protonation region,[5] as shown by the following argument. The protonation equilibrium of a base which follows an acidity function H_X is given by equation (1). Given values of ε_B and ε_{BH^+} the value of ε at any H_X may be calculated and a straight line drawn between the points for which $H_X = \mathrm{p}K - A$ and $H_X = \mathrm{p}K + A$. The gradient of this line decreases numerically as A increases; its value as a percentage of that at the pK is given in Table 1. The percentage of the total change in ε, that is of ($\varepsilon_{BH^+} - \varepsilon_B$), which occurs between $H_X = \mathrm{p}K - A$ and $\mathrm{p}K + A$ is also given. Within 0·4 H_X units of the pK the sigmoid curve is straight within *ca.* 5%; this region embraces over 40% of the total change in ε.¶

$$\log_{10} I = \mathrm{p}K - H_X \qquad (1)$$

$$I = [\mathrm{BH^+}]/[\mathrm{B}] = (\varepsilon - \varepsilon_B)/(\varepsilon_{BH^+} - \varepsilon) \qquad (2)$$

If sufficient experimental points are available around

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† For reviews see refs. 2.

‡ In ref. 2*a*, pp. 259–6, Hammett rewrites the equations of ref. 3 in a slightly more convenient form. However, some errors have been introduced: equation (56)[2a] should read $2\varepsilon_{\frac{1}{2}} = \varepsilon_B + \varepsilon_{BH^+} + H_0\,(G_B + G_{BH^+})$; the line before equation (58) should read 'with slope $-x$,' and equation (59) upper line should be $0{\cdot}87[2(\mathrm{d}\varepsilon/\mathrm{d}H_0)_{\frac{1}{2}} - (G_B + G_{BH^+})]$. We thank Professor Hammett for his agreement on these corrections.

¶ If the base follows an acidity function which is not equal to H_X, but varies linearly with it, equation (1) is replaced by $\log_{10} I = m(H_{\frac{1}{2}} - H_X)$, where $H_{\frac{1}{2}}$ replaces the term pK. The top line of Table 1 may be replaced by $0{\cdot}01/m$, $0{\cdot}1/m$, *etc.*, but the second and bottom lines remain unchanged.

[1] (*a*) K. L. Cook and A. J. Waring, following paper; (*b*) preliminary communications, K. L. Cook and A. J. Waring, *Tetrahedron Letters*, 1971, 1675, 3359.

[2] (*a*) L. P. Hammett, 'Physical Organic Chemistry,' McGraw-Hill, New York, 2nd edn., pp. 266—296; (*b*) C. H. Rochester, 'Acidity Functions,' Academic Press, London, 1970; (*c*) M. Liler, 'Reaction Mechanisms in Sulphuric Acid,' Academic Press, London, 1971.

[3] A. R. Katritzky, A. J. Waring, and K. Yates, *Tetrahedron*, 1963, **19**, 465.

[4] C. D. Johnson, A. R. Katritzky, B. J. Ridgewell, N. Shakir, and A. M. White, *Tetrahedron*, 1965, **21**, 1055.

[5] A. J. Waring, Ph.D. Thesis, Cambridge University, 1962.

the mid-point of the curve, a best straight line may be drawn or calculated (least squares) and the H_X and gradient of the sigmoid curve at half-protonation, with their standard errors, are available.

TABLE 1 (see text)

A, in H_X units	0·01	0·1	0·2	0·4	0·5	0·6
Gradient, % of maximum	100	100	98·3	94·8	91·2	87·7
% of ε change within $H_X = \mathrm{p}K \pm A$	1·2	11·4	22·4	43·0	52·0	59·8

Absorbance data were also transformed into straight line form using equations (2)—(4). Medium effects present difficulty in choosing values of ε_{BH^+} for equation (2); the sigmoid plots have shapes like those shown in refs. 3—5. The straight-line portion ('arm') which represents complete protonation may be extrapolated to lower acidities to give estimates of the cation absorbance at these acidities, and these ε_{BH^+} values are used for calculating the I value at each acidity. This method has been used in refs. 4, 6, and 7. The errors implicit in this extrapolation, and in the method of ref. 3 can introduce uncertainties, but the values should be more valid than any constant value of ε_{BH^+}. However, as a check on the possible size of errors involved we also used a single value of ε_{BH^+}, taken where the sigmoid curve and the cation 'arm' merge: the results agree quite closely. Weighted mean values of H_0[8] and H_A[9] at half-protonation, $(H_0)_{\frac{1}{2}}$ and $(H_A)_{\frac{1}{2}}$, and the corresponding slope parameters m_0 and m_A [see equations (3) and (4)] are in Table 2; the error limits embrace values derived from all the specified wavelengths and calculation methods.

TABLE 2

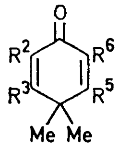
Compd.	Wave-lengths	$(H_0)_{\frac{1}{2}}$ [a]	m_0 [b]	$(H_A)_{\frac{1}{2}}$ [c]	m_A [d]	% H_2SO_4 [e]	pK [f]	Range of acids [g]
(1)	240 * 260	−3·15 ± 0·05 [h]	0·53 ± 0·03	−2·37 ± 0·03	1·03 ± 0·01	48·0 ± 0·03	−2·37 ± 0·03 (−2·41 ± 0·05)	35—60%
(2)	240 * 260 305 *	−2·44 ± 0·05	0·69 ± 0·03	−2·01 ± 0·03	1·13 ± 0·03	40·5 ± 0·6	−2·01 ± 0·03 (−2·11 ± 0·12)	16—55%
(3)	240 † 260 * 305 *	−2·39 ± 0·09	0·76 ± 0·04	−1·97 ± 0·06	1·12 ± 0·06	39·7 ± 1·1	−1·97 ± 0·06 (−2·09 ± 0·12)	19—59%
(4)	240 * 260 320 †	−1·56 ± 0·03	0·79 ± 0·04	−1·38 ± 0·02	1·05 ± 0·03	27·6 ± 0·4	−1·38 ± 0·02 (−1·40 ± 0·04)	6—42%
(5)	247 * 265 312 *	−2·25 ± 0·04	0·85 ± 0·03	−1·86 ± 0·04	1·28 ± 0·08	37·6 ± 0·6	−1·86 ± 0·04 (−2·06 ± 0·07)	11—48%
(6)	240 260 315 *	−2·99 ± 0·18 [i]	0·57 ± 0·01	−2·31 ± 0·10	1·07 ± 0·02	46·7 ± 1·8	−2·31 ± 0·10 (−2·40 ± 0·14)	31—55%

[a] Half-protonation acidity on Hammett's function H_0, using acidity scales of refs. 8. [b] See equation (3). [c] Half-protonation acidity on amide acidity function H_A, using scales of refs. 9. [d] See equation (4). [e] Half-protonation acidity (weight %). [f] Best estimates, based on H_A. Values in parentheses allow for $m \neq 1{\cdot}00$; see text. [g] Equations (3) or (4) are obeyed with the tabulated parameters over this range of acidity; weight %. [h] V. P. Vitullo, *J. Org. Chem.*, 1970, **35**, 3976 gives $(H_0)_{\frac{1}{2}} - 3{\cdot}66 \pm 0{\cdot}13$, m_0 $0{\cdot}62 \pm 0{\cdot}02$ based on 295 nm where there is a strong medium effect. [i] V. P. Vitullo, *J. Org. Chem.*, 1969, **34**, 224 gives m_0 $(H_0)_{\frac{1}{2}}$ *ca.* −2·1.

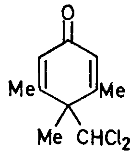
* Moderately strong medium effect at this wavelength. † Strong medium effect.

$$\log_{10} I = m_0[(H_0)_{\frac{1}{2}} - H_0] \qquad (3)$$

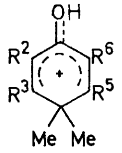
$$\log_{10} I = m_A[(H_A)_{\frac{1}{2}} - H_A] \qquad (4)$$



	R^2	R^3	R^5	R^6
(1)	H	H	H	H
(2)	H	Me	H	H
(3)	H	Et	H	H
(4)	H	Me	Me	H
(5)	Me	H	Me	H



(6)



(7)

DISCUSSION

For the thermodynamic pK of a base to be defined using an acidity function H_X equation (1) must be followed over the whole protonation range. In practice the quantity I cannot be found sufficiently accurately to test this requirement over more than about 1·3 H_X units on

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[6] C. C. Greig and C. D. Johnson, *J. Amer. Chem. Soc.*, 1968, **90**, 6453.

[7] (*a*) S. R. Hartshorn, R. B. Moodie, and K. Schofield, *J. Chem. Soc.* (*B*), 1971, 2454; (*b*) V. C. Armstrong and R. B. Moodie, *ibid.*, 1968, 275.

[8] Values of H_0 from large scale graphs of the data of K. N. Bascombe and R. P. Bell, *J. Chem. Soc.*, 1959, 1096; M. A. Paul and F. A. Long, *Chem. Rev.*, 1957, **57**, 1; and M. J. Jorgenson and D. R. Hartter, *J. Amer. Chem. Soc.*, 1963, **85**, 878. Use of the recently remeasured scale of C. D. Johnson, A. R. Katritzky, and S. A. Shapiro, *J. Amer. Chem. Soc.*, 1969, **91**, 6654 changes the $(H_0)_{\frac{1}{2}}$ values by less than 0·03; on the scale of P. Tickle, A. G. Briggs, and J. M. Wilson, *J. Chem. Soc.* (*B*), 1970, 65, the $(H_0)_{\frac{1}{2}}$ values are higher by 0·01 to 0·15.

[9] Values of H_A from (*a*) K. Yates, J. B. Stevens, and A. R. Katritzky, *Canad. J. Chem.*, 1964, **42**, 1957 extended by (*b*) C. D. Johnson, A. R. Katritzky, and N. Shakir, *J. Chem. Soc.* (*B*), 1967, 1235.

each side of the pK (see Table 2). Usually if equation (1) applies over this range for a series of related compounds of different basicities it is assumed that H_X is the appropriate acidity function. Most of the dienones we have studied follow most closely the amide acidity function H_A [9] [equation (4)], but have m_A values close to but not equal to unity. The discrepancies may reflect experimental uncertainties, or adherence to some other acidity function which is not quite identical to H_A. Other authors have assumed that m values within the range 0·79—1·25 [4,7b,10-12] are still consistent with adherence to the appropriate acidity function. We incline to this view for compounds (1)—(4) and (6); the $(H_A)_{\frac{1}{2}}$ values should then represent the closest estimates of thermodynamic pK values. An alternative approach, which has been frequently used, assumes that a base which follows equation (3) with a value m_0 actually follows a new acidity function which changes with acid concentration m_0 times as fast as does H_0. It is not necessarily valid, however, to use $m_0(H_0)_{\frac{1}{2}}$ as an accurate estimate of the thermodynamic pK because it is not certain that the new scale is identical with H_0 at a common value of zero and diverges uniformly therefrom. This is certainly not true of H_A, although it is for many other acidity scales.[2,13] Consideration of a graph of H_A against H_0 [13] shows that for a base which falls between H_0 and H_A behaviour, and closer to H_A as the dienones do, $m_0(H_0)_{\frac{1}{2}}$ or $m_A(H_A)_{\frac{1}{2}}$ will be somewhat inaccurate estimates of the pK, but that equation (5) should give better estimates. This assumes that the 'dienone acidity function' merges with H_0 and H_A near $-1{\cdot}0$ and that all three functions diverge uniformly from that point.* This procedure is applied to the values in Table 2 to give

$$\mathrm{p}K = (H_A)_{\frac{1}{2},\mathrm{corr.}} = m_A[(H_A)_{\frac{1}{2}} + 1{\cdot}0] - 1{\cdot}0 \qquad (5)$$

the values in parentheses in the pK column. The difference produced for compounds (1)—(4) and (6) is no more than 0·1 units, which is within the accuracy claimed [9] for the H_A scale. For (5), which falls evenly between H_0 and H_A behaviour the difference is larger.

An alternative empirical approach devised by Bunnett and Olsen [14] uses a plot according to equation (6). This

$$H_0 + \log I = \phi\,(H_0 + \log\,[\mathrm{Acid}]_{\mathrm{stoich.}}) + \mathrm{p}K \qquad (6)$$

method, when applied to amides whose pK values are defined by the H_A scale, gives discrepancies of *ca.* 0·3 units [14] which were originally attributed to incorrect anchoring of the H_A scale; later work [9b] supports the H_A scale as originally defined. The dienones (2) and (5) give Bunnett and Olsen plots with pronounced steps at $(H_0 + \log\,[\mathrm{Acid}])$ *ca.* $-1{\cdot}3$; extrapolation of the two straight portions of each graph gives pK estimates which differ by *ca.* 0·2 units. The lower acidity portion gives a pK value close to that defined by the H_A scale. The step in the plots is understandable. For an amide base to give a linear Bunnett and Olsen plot, a plot of $(H_0 - H_A)$ against $(H_0 + \log\,[\mathrm{Acid}])$ must be linear. This is so from $(H_0 + \log\,[\mathrm{Acid}])$ *ca.* $-5{\cdot}5$ to *ca.* $-1{\cdot}7$ for sulphuric acid, but there is then a region where $(H_0 - H_A)$ changes too slowly. The step cannot be reliably detected for the weaker bases (1) and (6) or the stronger base (4) because it would be in a region where the quantity I is least accurately known. Estimates of pK from the Bunnett and Olsen plots are not given here because of this weakness which would normally be detectable for only a few bases.

When this work was completed H_0 [15] but not H_A data were available for aqueous perchloric acid. Limited studies showed the data from spectra in perchloric acid to fit onto the sulphuric acid sigmoid curves of ε *vs.* H_0. Thus the $(H_0)_{\frac{1}{2}}$ and m_0 values agree in the two acids. More recently some H_A data have appeared,[16] and they also lead to satisfactory agreement. Thus $(H_A)_{\frac{1}{2}}$ for (1) is $(-2{\cdot}48 \pm 0{\cdot}05)$ in $HClO_4$ and $(-2{\cdot}38 \pm 0{\cdot}03)$ in H_2SO_4, and our results support the published H_A data within *ca.* 0·1 unit.

The adherence to the H_A function of most of the compounds discussed here is of interest. Similar adherence has been reported for many cyclohex-2-enones,[17] cyclopent-2-enones,[17a] and other αβ-unsaturated aldehydes, ketones, and carboxylic acids,[18,19] and benzaldehydes, benzoic acids, acetophenone, benzophenones,[18] primary[7b] and secondary [10] amides, carbamate esters,[7b] hydroxamic esters,[12] aliphatic esters,[20] pyridine *N*-oxides,[9b] and sulphoxides.[20] For most of these bases protonation may occur predominantly at a carbonyl oxygen atom † and the charge be delocalised by an adjacent double-bond, phenyl ring, or amino-group. Some cyclohexa-

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* This is not true over the whole acidity range, because the graph of H_A against H_0 resembles three intersecting straight lines, but it is the best approximation over the acidities with which we are concerned.

† For proof that the predominant cations from the cyclohexa-2,5-dienones have the hydroxyarenium ion structures (7), see ref. 21. The n.m.r. of the cation of (4) in 70% D_2SO_4–D_2O shows no exchange of the vinyl protons within 75 h at 37—38 °C, showing that no significant protonation occurs at C-2. The n.m.r. in 70% H_2SO_4 shows no trace of peaks other than those due to (7), and no evidence of protonation at C-3. For similar evidence of carbonyl oxygen protonation of other αβ-unsaturated ketones; see refs. 22.

[10] D. W. Farlow and R. B. Moodie, *J. Chem. Soc.* (*B*), 1970, 334.

[11] D. Landini, G. Modena, G. Scorrano, and F. Taddei, *J. Amer. Chem. Soc.*, 1969, **91**, 6703.

[12] A. J. Buglass, K. Hudson, and J. G. Tillett, *J. Chem. Soc.* (*B*), 1971, 123.

[13] K. Yates and R. A. McClelland, *J. Amer. Chem. Soc.*, 1967, **89**, 2686.

[14] J. F. Bunnett and F. P. Olsen, *Canad. J. Chem.*, 1966, **44**, 1899.

[15] K. Yates and H. Wai, *Canad. J. Chem.*, 1964, **86**, 5408.

[16] Unpublished work of K. Yates, reported in ref. 11.

[17] (*a*) R. I. Zalewski and G. E. Dunn, *Canad. J. Chem.*, 1969, **47**, 2263; (*b*) R. I. Zalewski and G. E. Dunn, *ibid.*, 1970, **48**, 2538.

[18] R. I. Zalewski and G. E. Dunn, *Canad. J. Chem.*, 1968, **46**, 2469.

[19] T. S. Sorenson, personal communication cited in ref. 18.

[20] J. Siigur, V. Toomes, E. Soonike, H. Kuura, and U. Haldna, *Reakts. spos. org. Soedinenii*, 1970, **7**, 412 (*Chem. Abs.*, 1970, **73**, 130,524).

[21] K. L. Cook, M. J. Hughes, and A. J. Waring, *J.C.S. Perkin II*, 1972, 1506.

[22] J. N. Marx, *Tetrahedron Letters*, 1971, 4957; G. A. Olah, Y. Halpern, Y. K. Mo, and G. Liang, *J. Amer. Chem. Soc.*, 1972, **94**, 3554.

2,5-dienones do not, however, seem to follow H_A despite having normal cations of type (7).[23]

Zalewski and Dunn formulated an empirical additive relationship which correlates the pK of cyclohex-2-enones with their substitution pattern. Our results show that converting an alkyl substituted cyclohex-2-enone into the cyclohexa-2,5-dienone increases its basicity by (0·76 ± 0·08) unit; * an α- or β-methyl group on the new double bond is base strengthening by 0·25 or 0·75 unit, respectively, as in the cyclohexenones.[17]

TABLE 3

U.v. data on dienones and their cations

Compd.	Charge on species [a]	Solvent	$\lambda_{max.}$/nm	log ε
(1)	0 [b]	H_2O	240	4·189
		n-Hexane	224	4·187
		iso-octane	225	4·182
	+ [c]	67—78% H_2SO_4	260	4·144
			290 [d,e]	4·077
(2)	0	H_2O	241	4·172
		n-Hexane	227	4·151
		iso-octane	227	4·151
	+ [c]	68—79% H_2SO_4	260	4·167
			305 [d,f]	3·783
(3)	0	H_2O	242	4·182
		95% EtOH	238	4·175
	+ [c]	63—71% H_2SO_4	260	4·168
			305 [d,g]	3·778
(4)	0	H_2O	246	4·251
		n-Hexane	230·5	4·222
		iso-octane	230·8	4·212
	+	73—83% H_2SO_4	261	4·242
			314 [d,e]	3·884
(5)	0	H_2O	246·5	4·177
	+ [c]	71% H_2SO_4	266	4·145
			315 [d,g]	3·735
(6)	0 [h]	H_2O	244	4·228
	+ [h]	73—90% H_2SO_4	264	4·212
			318 [d,i]	3·807

[a] 0 = neutral dienone; + = cation of structural type (7). [b] Lit.: H_2O, 238 nm, log ε 4·15, V. P. Vitullo and N. Grossman, *Tetrahedron Letters*, 1970, 1559; EtOH, 234·5 nm, log ε 4·16, E. W. Garbisch, *J. Org. Chem.*, 1965, **30**, 2109; 95% EtOH, 234 nm, log ε 4·12, G. Legler and B. Quiring, *Tetrahedron*, 1967, **23**, 2683. [c] Calculated at zero time from kinetic experiments. [d] This peak shows a strong medium effect. [e] The values given are for 75% H_2SO_4. [f] Values in 78% H_2SO_4. [g] Values in 71% H_2SO_4. [h] Lit.: H_2O, 242 nm, log ε 4·238; 90·5% H_2SO_4, 263, 320 nm, log ε 4·220, 3·841, V. P. Vitullo, *J. Org. Chem.*, 1969, **34**, 224. [i] Values in 80% H_2SO_4.

The one notable exception to this correlation is the 4,4-dimethyldienone (1), which has pK *ca.* −2·40 instead of the calculated value of *ca.* (−2·8 ± 0·1). The finding that the 3-ethyl group in (3) is only slightly more base strengthening than the 3-methyl group in (2) agrees with Zalewski and Dunn's finding that these groups are equally base strengthening in cyclohex-2-enones (within 0·05 unit). It supports a recent conclusion that, ' methyl and ethyl groups are approximately equally effective in stabilising arenium ions '[24] in contrast with a report that methyl groups are distinctly better in this role (by *ca.* ΔH 2·5 kcal mol^{-1}).[25]

EXPERIMENTAL

The cyclohexadienones were those used in ref. 21. The liquids (1) and (2) were purified by preparative g.l.c. on a cyanoethylsilicone gum XF1150, and (2) and (5) by column chromatography on alumina (Spence, type H), followed in each case by re-drying ($CaSO_4$) and molecular distillation to final purities of >99·9, >99·7 and >97% for (1), (2) and (5), respectively. Purities were checked by g.l.c. at greatly enhanced sensitivity on silicone E30, polyethyleneglycol adipate and neopentylglycol succinate columns. Solid (3) was purified by alumina chromatography, then recrystallisation from light petroleum (b.p. 40—60°) and molecular distillation to m.p. 42·5—43°, and was ⩾99% pure by g.l.c.; (4) was recrystallised (b.p. 40—60° petroleum) then sublimed to m.p. 46·5—47·3° and purity ⩾99% by g.l.c.; (6) was crystallised (b.p. 80—100° petroleum) and then sublimed to m.p. 106·2—106·5°. All samples have satisfactory microanalytical, i.r., u.v., n.m.r., and mass spectroscopic data.

U.v. spectra were recorded on a Cary 14 instrument with cell compartment thermostatted at 25 ± 0·1 °C. Acids were made by diluting M.A.R. quality H_2SO_4 or $HClO_4$ (Hopkin and Williams) and their densities, obtained by density balance, converted into weight % using graphs of data from International Critical Tables. For acids up to *ca.* 50%, 1 ml of a thermostatted aqueous solution of dienone was diluted to 10 ml using the thermostatted acid and the final weight % read off a graph constructed according to the footnote.† For stronger acids the heat of mixing was significant and could lead to unacceptable kinetic plots: a sample of dienone weighed on a microanalytical balance was dissolved directly in 50 or 100 ml of the acid. The dilution and direct-weighting methods gave perfectly overlapping results. For dienones which rearranged at noticeable rates the absorbances at the time of mixing were calculated from the kinetic data (see following paper). Checks of Beer's law gave ε values within 1% over concentration factors of 8—10 times.

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* This is also true for the bicyclic and other dienones which we have studied.[23]

† If x ml of P_0% sulphuric acid (density d_0 in g ml^{-1}) and 1·0 ml of water (density d_{H_2O}) are mixed to give 10·0 ml of P_1% acid (density d_1), then $P_0 = 10\ P_1d_1/(10d_1 - d_{H_2O})$. For arbitrarily chosen values of P_1 the d_1 values are available, and P_0 is then calculated (at 25 °C throughout).

[23] M. J. Hughes and A. J. Waring, to be published.

[24] D. M. Brouwer and J. A. van Doorn, *Rec. Trav. chim.*, 1970, **89**, 88.

[25] E. M. Arnett and J. W. Larsen, *J. Amer. Chem. Soc.*, 1969, **91**, 1438.