Adaptation of Characteristic Vector Analysis to pK_{BH^+} Calculations of Very Weak Bases from Incomplete Ultraviolet Spectral Data

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An adaptation of characteristic vector analysis has been applied to incomplete u.v. spectral data of a very weak base only partially protonated in pure sulphuric acid, 3-cyano-5,5-dimethylcyclohex-2-en-1-one (1). The estimated pK_{BH^+} value, −5.29, obtained from the H_A acidity function is in very good agreement with those calculated from linear free energy relationships: pK_{BH^+} *vs.* σ^+ (−4.96) or pK_{BH^+} *vs.* σ_I, σ_R^+ (−4.93) and the extra-thermodynamic relationship of pK_{BH^+} *vs.* $\Delta H^\circ_{BF_3}$ (−5.32) for a series of 3-substituted-5,5-dimethylcyclohex-2-en-1-ones. This statistical method can be generalized for compounds in which the protonation is very incomplete even in pure sulphuric acid and for which the u.v.–visible spectral data are limited.

Evaluation of the relative basicities of weak organic bases B has attracted much interest both as a source of information about electronic structures and as a means of interpreting the reactivities of acid-catalysed reactions.[1–6] In the solution phase, the most common measure of basicity is the pK_{BH^+} of the conjugate acid BH$^+$ of the base B [equation (1)].[1] If the main problem in evaluating thermodynamic pK_{BH^+} values in non-ideal media is the choice of methods to solve equation (2)[7,8]

$$B + H^+ \xrightleftharpoons{K_{BH^+}} BH^+ \qquad (1)$$

$$pK_{BH^+} = \log I - \log C_{H^+} - \log(\gamma_B\gamma_{H^+}/\gamma_{BH^+}) \qquad (2)$$

where I is the ionization ratio (C_{BH^+}/C_B) and γ the molar activity coefficients, the first requirement for all methods is that measurements are made under conditions where significant amounts of the unprotonated and protonated forms of the base are present simultaneously in solution. Moreover, the characteristic parameters of the protonated form BH$^+$ (for instance, ε_{BH^+} for the u.v. method or ν_{BH^+} for the n.m.r. method) often require the determination of the ionization ratio, whatever the spectroscopic method. However, obtaining of these paramaters for a very weak base is sometimes difficult because the base is incompletely protonated even in 100%-H_2SO_4 or other acids. This problem frequently occurs with simple aliphatic ketones which are only 50%-protonated in *ca.* 80%-H_2SO_4, and the estimated pK_{BH^+} values of which differ considerably from those reported.[9–12] In the course of our study of Brønsted and Lewis basicities of cyclohexenones[7,13–16] we encountered this problem for compounds with strongly electron-withdrawing substituents on the ethylenic double bond, particularly for 3-cyano-5,5-dimethylcyclohex-2-en-1-one (1), for which 50%-protonation was not observed in 98%-sulphuric acid solution. The encouraging results we obtained using characteristic vector analysis (CVA) for the correction of 'medium effects' from u.v. spectral data[7,17] and for examination of acidity functions[8] prompted us to adapt this method to estimate the pK_{BH^+} value of (1) from very incomplete u.v. spectral data of this compound.

Experimental

Substrate.—The preparation of 3-cyano-5,5-dimethylcyclohex-2-en-3-one (1) and its spectroscopic properties are described.[18,19]

General Procedure for Spectrophotometric Basicity Determination.—Methods for pK_{BH^+} measurement have been previously reported.[7]

Principal Component Analysis of Spectra.—The experimental u.v. spectra of sulphuric acid solutions of 3-cyano-5,5-dimethylcyclohex-2-en-1-one (1) presented in Figure 1 are very incomplete. Only the spectra 14—18 recorded in non-aqueous solutions with $H_A < -5$ show shoulders in the long-wavelength region, which could be characteristic for the protonated form, BH$^+$, of the ketone (1). The ionization ratio $I = [B]/[BH^+]$ could not be calculated from such spectral data, even using CVA–TCA procedure,[17] because the range of the magnitude A_{BH^+} is not known. We attempted to overcome this serious problem using principal component analysis (PCA) procedures, claimed as the method for the calculation of physical responses of two pure forms from data obtained from mixtures of the two components.[20,21] The first objective of PCA

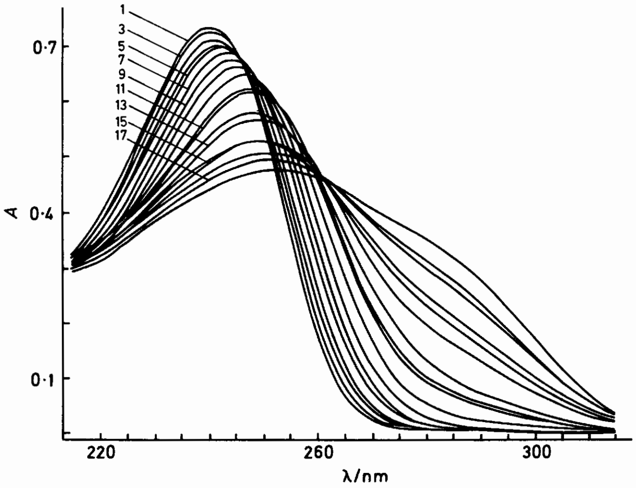

Figure 1. Experimental absorbances of (1) as a function of sulphuric acid acidity (H_A). Solvent numbers (top to bottom at $\lambda_{max.}$ = 240) and H_A are: (1) +1.00; (2) +0.09; (3) −0.92; (4) −1.64; (5) −2.14; (6) −2.64; (7) −3.01; (8) −3.45; (9) −3.86; (10) −4.30; (11) −4.32; (12) −4.52; (13) −4.75; (14) −4.92; (15) −4.99; (16) −5.24; (17) −5.42, and (18) −5.70

or CVA is to obtain an 'abstract' solution, wherein all data are expressed as linear sums of product terms. The number of terms is called the number of components (or vectors). The standard PCA or CVA procedures applied to the digitalized set of spectra shown in Figure 1 indicate two principal components accounting for 99.50% of total data variability. Thus any absorbance $A_{n,p}$ could be represented by the following equation:

$$A_{n,p} = C_{1,p}\,L_{n,1} + C_{2,p}\,L_{n,2} \qquad (3)$$

In this equation C represents the principal component for wavelength p, and L represents the loading for the nth spectrum. The 'abstract' solution is purely mathematical and is devoid of physical meaning; however we can reconstitute the new family of absorption spectra, as shown in Figure 2. The isosbestic point is now much more clearly defined and the maximum of spectrum 18 is shifted towards the long-wavelength region characteristic for protonated base.

The ultimate objective of PCA is to convert the 'abstract' solution into a real solution and to develop a meaningful model based on the data. Transformation of the 'abstract' solution, which is presented as a plot of orthogonal principal components $C_{1,p}$ *vs.* $C_{2,p}$ in Figure 3, into real spectra is achieved by determining the new oblique axes. It was proposed[20] that the asymptotes D,E starting from origin would enable us to find the real solution under certain conditions: (*i*) absorbances (and concentrations) of both components, B and BH^+ being non-negative, and (*ii*) the absorbance of each component reaches zero, at the wavelength equivalent to the tangential point. The real components $C_{D,p}$ and $C_{E,p}$, and equivalent loadings allow us to calculate the spectra of BH^+ and B, respectively. The second condition however has been discarded[21] and replaced by the highest dissimilarity of real spectra (HDRS).

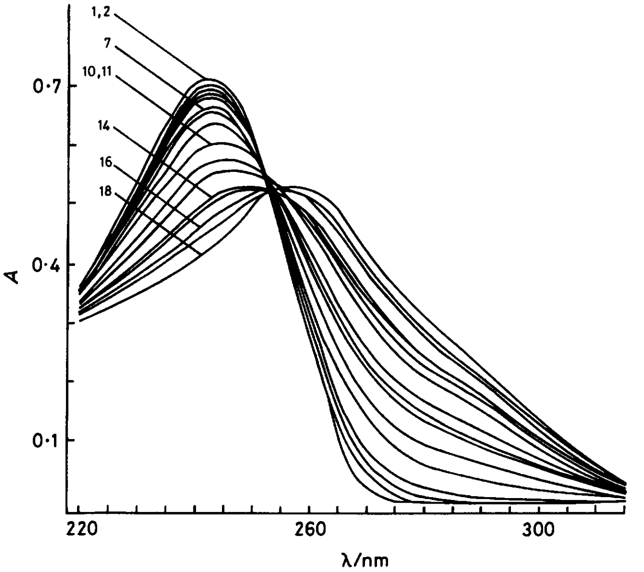

Figure 2. Reconstituted absorbances of (1). For further details see Figure 1

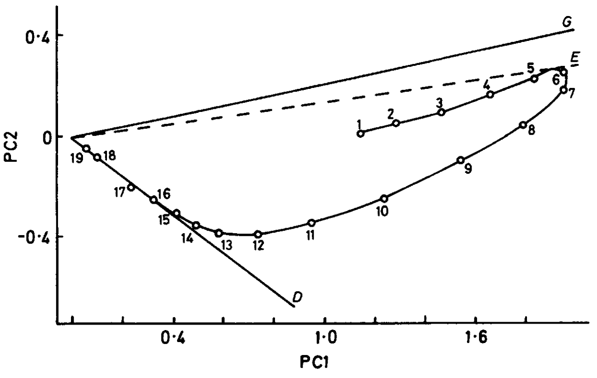

Figure 3. The 'abstract' solution as a plot of principal components. *D*, *E*, and *G* are the oblique axes (see text). The numbers refer to wavelengths in the region 220—310 nm at 5 nm intervals

Results and Discussion

Both procedures[20,21] give good approximations of the pure base spectrum B. The shape of the absorption band is regular with $\lambda_{max.}$ 246 nm and absorbance A_B 0.665. The absorbance is lower than for spectra 1—6. This means that the base under study undergoes solvation in highly aqueous solutions rather than measurable protonation. Such an explanation is rational and obvious.[22] However the procedures[20] fail, in our opinion, to predict the spectrum of the ion BH^+. The projection of abstract principal components on the oblique axis *E* yields the spectrum of BH^+ with $A = 0$ at λ 242.5 and 275 nm with very high absorbance (1.1). The shape of this spectrum is rather strange especially in the short-wavelength region.

We believe that the HDRS procedure,[21] in which the projection axis for BH^+ would be beyond the axis *E* and must fulfill the conditions $|\lambda^{B}_{max.} - \lambda^{BH^+}_{max.}| = max.$ and $A_{BH^+} > 0$, gives good results. The best solution was found with axes *D* and *G* ($\angle$ G-O-PC1 = 11.5°), and the spectra of B and BH^+ calculated from these are presented in Figure 4.

The ionization ratio and pK_{BH^+} value were calculated using the 'generalized Hammett method' described previously,[7] and supported by earlier works.[13,23,24] Two $\lambda_{max.}$ values were used: λ_B 245 and λ_{BH^+} 270 nm to calculate ΔA_B, ΔA_{BH^+}, and ΔA_n where ΔA is the difference in optical density in λ_B and λ_{BH^+} for the appropriate spectra. Thus the ionization ratio *I* and pK_{BH^+} were calculated from equations (4) and (5). The H_A acidity

$$I = (\Delta A_{BH^+} - \Delta A_n)/(\Delta A_n - \Delta A_B) \qquad (4)$$

$$pK_{BH^+} = H_A + \log I \qquad (5)$$

function corrected by Edward and Wong[25] was used. The main results are presented in the Table.

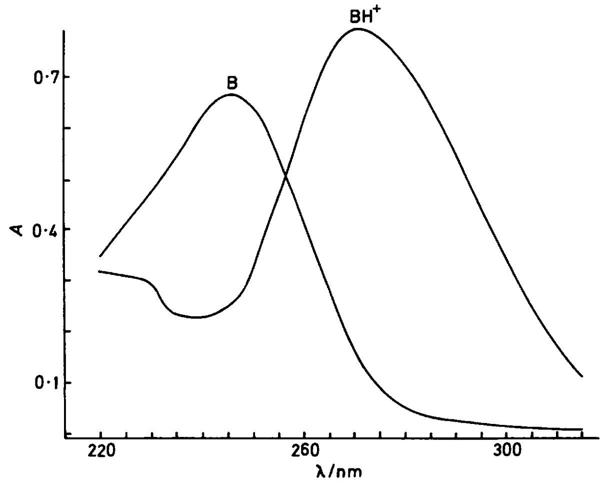

Figure 4. Calculated spectra of B and BH^+

Table. Abbreviated experimental data for the pK_{BH^+} calculation

Spectrum	$-H_A$	ΔA_n[a]	log I	pK_{BH^+}
B		−0.4994[b]		
9	4.3024	−0.4049	−0.9852	−5.2876
10	4.3204	−0.3987	−0.9546	−5.2750
11	4.5233	−0.3335	−0.7054	−5.2287
12	4.7475	−0.2556	−0.4960	−5.2435
13	4.9233	−0.1959	−0.3656	−5.2889
14	4.9899	−0.1701	−0.3139	−5.3004
BH$^+$		0.5084[c]		
			mean	−5.27 ± 0.03

[a] $\Delta A_n = A_{n,p=275\,nm} - A_{n,p=240\,nm}$. [b] ΔA_B calculated using $A_{B,p=275\,nm} = 0.1524$, $A_{B,p=240\,nm} = 0.6518$. [c] ΔA_{BH^+} calculated using $A_{BH^+,p=275\,nm} = 0.7448$, $A_{BH^+,p=240\,nm} = 0.2364$.

The mean value found for pK_{BH^+} was −5.27 units, standard deviation ±0.03. The slope of the straight line

$$\log I = -mH_A + b \qquad (6)$$

$m = 0.97 \pm 0.05$ means that the amide acidity function H_A describes the protonation of (**1**) correctly. The intercept b, −5.29 (the value of H_A at 50%-protonation, $c_B = c_{BH^+}$), is in close agreement with pK_{BH^+}.

The calculated value of pK_{BH^+} (−5.27) is in fairly good agreement with that calculated from LFER based on σ^+ substituent constant (−4.96) or on σ_I and σ_R^+ substituent constants (4.93) and in very good agreement with that estimated from the extra-thermodynamic relationship using the $\Delta H^\circ_{BF_3}$ basicity parameter (−5.32) for similar cyclohexenones.[16]

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