# Thermodynamics of Protonation of Substituted Pyridines in Aqueous Solutions

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The $pK_a$ values of 23 pyridinium ions have been calculated by observing the change in the n.m.r. chemical shift on deprotonation. The values for $\Delta G$, $\Delta H$, and $\Delta S$ have been obtained for this deprotonation from the $pK_a$ values at more than one temperature. The Hammett plot of the ionization values indicates that the $pK_a$ of a substituted pyridine can be estimated by the equation $pK_a = 5{\cdot}35 - 5{\cdot}23\Sigma\sigma$.

WHEN heterocyclic bases are dissolved in a protic solvent such as water, equilibrium (1) is established. The rates of the forward and reverse reactions are considerably higher than can be measured on the n.m.r. time scale. This rapid exchange would afford only one set of proton signals in the n.m.r. spectrum at a position which is determined by the ratio of the cationic and uncharged species. The observed chemical shift of a proton can be

(1)

expressed by equation (2) where $\nu_+$ and $\nu$ are the chemical

$$\nu_{\text{obs}} = \nu_+ p_+ + \nu p \qquad (2)$$

shifts of the cationic and uncharged forms respectively, while $p_+$ and $p$ represent the fractional populations of these two forms. At very low pH, it can be assumed that nearly all the pyridine is in the charged form, while at very high pH nearly all the material is in the uncharged form. An arbitrary assignment of 0 to the value of $\nu$ allows the calculation of $p_+$ from equation (2).

The standard ionization expression representing equation (1) can be modified to involve the ratio of $p_+/p$ instead of the concentrations as shown in equation (3). Thus, the exact observed chemical shift of a set of protons and the pH associated with this chemical shift can be

$$\text{p}K_{\text{a}} = \text{pH} + \log\,(p_+/p) \qquad (3)$$

used to calculate the p$K_a$ values of the pyridinium ions. Similar studies at various temperatures would then enable one to determine the thermodynamic functions of these bases. The effects of protonation on the chemical shifts of the ring protons and any protons on the substituent group can also be determined, and from these structure–reactivity relationships can be derived. The reliability of the n.m.r. method for evaluation of these functions has been verified by various authors.[1-4] One great advantage of this method of calculating data lies in the fact that the actual reagent concentration does not occur in equation (2) since only the ratio $(p_+/p)$, is determined from the n.m.r. spectra. As long as the ionic strength is kept constant, the reagent concentration may vary to a great extent without changing the p$K_a$ or the thermodynamic functions. In order to test the validity of this assumption, the concentration was varied by a factor of 2 but the ionic strength was kept constant at 1·0M. The values for the observed chemical shifts were within experimental error. Calculation of the p$K_a$ values at different temperatures allowed the evaluation in the usual way of the changes in $\Delta S$, $\Delta H$, and $\Delta G$ during the dissociation.

TABLE 1

N.m.r. chemical shifts [a] of the ring protons of various pyridines at 37 °C

| Substituted | $\nu_{BH^+}$/Hz | | | | $\nu_B$/Hz | | | | $\Delta\nu$/Hz | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 4-Br | | 307·8 | 327·8 | | | | 266·2 | 308·3 | | | 41·6 | 19·5 |
| 4-Cl | | 297·3 | 334·7 | | | | 254·7 | 311·5 | | | 42·6 | 23·2 |
| 4-CHO | | 296·2 | 336·0 | | | | 265·8 | 325·5 | | | 30·4 | 10·5 |
| 4-$CO_2H$ | | 306·3 | 341·2 | | | | 274·0 | 327·0 | | | 32·3 | 14·2 |
| 4-Ac | | 315·8 | 349·0 | | | | 270·7 | 325·5 | | | 45·1 | 23·5 |
| 4-CN | | 317·7 | 352·8 | | | | 272·3 | 331·7 | | | 45·4 | 21·1 |
| 4-SH | | 280·6 | 313·0 | | | | 249·5 | 288·0 | | | 31·1 | 25·0 |
| 4-$NH_2$ | | 214·7 | 284·5 | | | | 208·0 | 290·0 | | | 6·7 | 5·5 |
| 4-Me | | 281·5 | 325·0 | | | | 237·0 | 304·7 | | | 44·5 | 20·3 |
| 4-$NMe_2$ | | 218·3 | 287·5 | | | | 203·0 | 290·0 | | | 15·3 | 2·5 |
| 4-NHMe | | 297·2 | 342·0 | | | | 252·7 | 318·5 | | | 44·5 | 23·5 |
| 3-Me | 323 | 314·0 | 283·0 | | | 295·0 | 247·0 | 230·0 | | 28·0 | 67·0 | 53·0 |
| 3-CN | 307·4 | 343·1 | 348·2 | 365·7 | 267·6 | 296·4 | 321·4 | 334·0 | 39·8 | 46·7 | 26·8 | 31·7 |
| 3-Cl | 300·3 | 328·9 | 336·2 | 344·7 | 259·2 | 281·0 | 313·5 | 316·7 | 41·1 | 47·9 | 22·7 | 28·0 |
| 3-Ac | 306·1 | 348·1 | 355·2 | 368·5 | 262·2 | 380·1 | 331·0 | 349·3 | 43·9 | 40·0 | 24·2 | 19·2 |

[a] Average experimental error in determining chemical shifts is <1 Hz. Shifts relative to $Me_4NCl$ as internal standard.

## EXPERIMENTAL

3-Acetylpyridine was prepared by the method of La Forge.[5] All other pyridines were supplied by Aldrich Chemical Company and used without further purification. $^1$H N.m.r. spectra were obtained at 60 MHz using a Varian variable-temperature control unit V6057. The chemical shifts were measured with tetramethylammonium chloride as internal standard. For all but a few compounds, the spectra consisted of symmetrical bands. The chemical shifts were determined by inspection. In the cases where the spectra were not highly symmetrical, the spectra were analysed by a PDP/8I computer. The noniterative ' n.m.r. simulation ' program was obtained from the Digital Equipment Corporation. The computed chemical shifts agreed with the input chemical shifts within 1 Hz. A pH measurement was performed using a Corning pH meter. Ionic strengths of all test solutions were 1·0M.

*Typical Determination.*—A sample of between 0·001 and 0·0015 mol of the base or its hydrochloride was dissolved in 1·0M-hydrochloric acid (25 ml). The solution (15 ml) was added to a 1·0M-tetramethylammonium chloride solution (1 ml). The pH was determined, a sample was placed in an n.m.r. tube, and the pH was adjusted with 1·0M-NaOH solution (the pyridine served as its own buffer). The pH was redetermined and the operation was repeated until the pH of the sample solution was *ca.* 13. The n.m.r. spectra of the various samples were calculated relative to the internal standard.

The plot of pH *vs.* the chemical shift for the pyridines resulted in smooth curves similar to those reported by Leyden and Waters [6] for the ν–pH dependence of the n.m.r. spectra of mercaptosuccinicic acid. In all cases, at least 10 points were obtained in the area of rapidly changing chemical shift. Each p$K_a$ value reported is the result of at least two determinations. The chemical shifts from these two runs fell within experimental error.

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[1] J. F. Hinton and E. S. Amis, *Chem. Rev.*, 1967, **67**, 367.

[2] M. W. Mosher, C. B. Sharma, and M. R. Chakrabarty, *J. Magnetic Resonance*, 1972, **7**, 247.

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

[4] J. W. Pullen, J. Billheimer, and M. R. Chakrabarty, 157th National Meeting of the American Chemical Society, Minneapolis, Minnesota, April, 1969.

[5] F. B. La Forge, *J. Amer. Chem. Soc.*, 1928, **50**, 2479.

[6] D. E. Leyden and D. B. Waters, *Spectrochim. Acta*, 1969, **25A**, 1809.

TABLE 2

$\mathrm{p}K_\mathrm{a}$ Values for various pyridines

| Substituent | Temp. (°C) [a] 0 | 15 | 37 | 60 | 70 | 25 [b] |
|---|---|---|---|---|---|---|
| 4-Ac | | 3·70 ± 0·06 | 3·58 ± 0·07 | | 3·00 ± 0·04 | 3·62 |
| 3-Ac | 3·44 ± 0·07 | | 3·21 ± 0·20 | 3·03 ± 0·30 | | 3·26 |
| 4-NH$_2$ | 9·96 ± 0·01 | | 9·19 ± 0·02 | | | 9·68 |
| 4-Br | 4·20 ± 0·02 | 4·15 ± 0·07 | 3·96 ± 0·09 | | | 4·05 |
| 4-Cl | 4·26 ± 0·08 | 4·10 ± 0·19 | 4·09 ± 0·11 | | | 4·11 |
| 3-Cl | 2·98 ± 0·17 | | 2·86 ± 0·03 | 2·69 ± 0·03 | | 2·88 |
| 4-CN | | 2·38 ± 0·03 | 2·14 ± 0·02 | | 1·62 ± 0·05 | 2·26 |
| 3-CN | 1·63 ± 0·08 | | 1·56 ± 0·06 | 1·58 ± 0·01 | | 1·59 |
| 4-NMe$_2$ | 10·11 ± 0·07 | | 9·74 ± 0·10 | 8·74 ± 0·05 | | 9·47 |
| 4-CO$_2$H [c] | | 4·67 ± 0·11 | 4·60 ± 0·12 | | 4·07 ± 0·10 | 4·61 |
| 2,4-Me$_2$ | 7·14 ± 0·16 | | 6·46 ± 0·20 | | 6·04 ± 0·06 | 6·68 |
| 2,5-Me$_2$ | 6·63 ± 0·19 | | 6·18 ± 0·07 | | 5·59 ± 0·13 | 6·25 |
| 2,6-Me$_2$ | 7·35 ± 0·08 | | 6·67 ± 0·04 | | 5·92 ± 0·09 | 6·81 |
| 3,4-Me$_2$ | 6·52 ± 0·18 | | 6·28 ± 0·21 | | 5·55 ± 0·13 | 6·23 |
| 3,5-Me$_2$ | 6·55 ± 0·14 | | 5·85 ± 0·35 | | 5·23 ± 0·07 | 6·03 |
| 4-SH | 1·36 ± 0·03 | | 1·65 ± 0·02 | | | 1·56 |
| 4-CH$_2$NH$_2$ | 4·39 ± 0·11 | | 4·42 ± 0·09 | | | 4·41 |
| 3-CO$_2$H | 4·23 ± 0·16 | | 4·19 ± 0·04 | | 3·27 ± 0·28 | 3·98 |
| 2-Me | 6·41 ± 0·67 | | 5·65 ± 0·11 | 5·40 ± 0·06 | | 5·91 |
| 3-Me | 6·02 ± 0·09 | | 5·52 ± 0·04 | 5·30 ± 0·09 | | 5·68 |
| 4-Me | 6·50 ± 0·14 | | 5·88 ± 0·35 | 5·52 ± 0·13 | 5·32 ± 0·07 | 6·04 |
| 4-CHO | 5·20 ± 0·04 | | 4·72 ± 0·37 | | | 4·86 |
| H | 5·60 ± 0·07 | | 5·35 ± 0·08 | | 4·68 ± 0·02 | 5·31 |

[a] All ±1·5 °C. [b] Calculated from least squares. [c] Saturated solution.

RESULTS

The results of the measurements and the values of the acidity constants for the pyridinium ions are reported in Table 1. The $\mathrm{p}K_\mathrm{a}$ values at 25 °C in Table 1 were obtained by interpolation. Some values for the $\mathrm{p}K_\mathrm{a}$ of these pyridinium ions have been reported [7,8] at one of the temperatures used in this study. Our values for the $\mathrm{p}K_\mathrm{a}$ at this temperature are in excellent agreement with those reported. The interpolated values for the $\mathrm{p}K_\mathrm{a}$ at 25 °C are also within the experimental range of the published data.

TABLE 3

Thermodynamic properties for various pyridines [a]

| Substnt. | $\Delta G$/ kcal mol$^{-1}$ | $\Delta H$/ kcal mol$^{-1}$ | $-\Delta S$/ cal mol$^{-1}$ K$^{-1}$ [b] |
|---|---|---|---|
| 4-Ac | 5·18 ± 0·25 | 3·71 ± 0·23 | 4·03 |
| 3-Ac | 4·48 ± 0·15 | 2·40 ± 0·20 | 6·99 |
| 4-NH$_2$ | 12·91 ± 0·31 | 5·23 ± 0·20 | 24·30 |
| 4-Br | 5·36 ± 0·11 | 2·38 ± 0·14 | 10·0 |
| 4-Cl | 5·54 ± 0·27 | 2·57 ± 0·17 | 9·97 |
| 3-Cl | 3·96 ± 0·16 | 1·63 ± 0·17 | 7·82 |
| 4-CN | 2·95 ± 0·09 | 3·04 ± 0·13 | −0·30 |
| 3-CN | 2·21 ± 0·20 | 5·59 ± 0·17 | −1·13 |
| 4-NMe$_2$ | 13·19 ± 0·16 | 9·53 ± 0·03 | 1·23 |
| 4-CO$_2$H | 6·35 ± 0·19 | 8·14 ± 0·18 | −0·60 |
| 2,4-Me$_2$ | 8·93 ± 0·11 | 6·91 ± 0·11 | 6·79 |
| 2,5-Me$_2$ | 8·60 ± 0·30 | 5·59 ± 0·80 | 10·11 |
| 2,6-Me$_2$ | 9·32 ± 0·12 | 7·93 ± 0·70 | 4·49 |
| 3,4-Me$_2$ | 8·58 ± 0·08 | 4·11 ± 0·18 | 15·00 |
| 3,5-Me$_2$ | 8·24 ± 0·07 | 7·82 ± 0·51 | 1·41 |
| 4-SH | 2·06 ± 0·29 | −3·01 ± 0·03 | 17·01 |
| 4-CH$_2$NH$_2$ | 5·93 ± 0·27 | −0·31 ± 0·04 | 20·93 |
| 3-CO$_2$H | 5·45 ± 0·13 | 3·34 ± 0·30 | 7·07 |
| 2-Me | 8·09 ± 0·13 | 7·14 ± 0·46 | 2·40 |
| 3-Me | 7·80 ± 0·20 | 4·87 ± 0·13 | 9·84 |
| 4-Me | 8·30 ± 0·06 | 6·54 ± 0·43 | 5·91 |
| 4-CHO | 6·61 ± 0·08 | 4·82 ± 0·02 | 6·02 |
| H | 7·10 ± 0·25 | 4·00 ± 0·11 | 10·39 |

[a] Calculated at 25 °C. [b] Average *ca.* 1·5 cal mol$^{-1}$ K$^{-1}$.

The values obtained for the chemical shifts of the charged and uncharged species are normally quite different, with the protons of the charged form appearing downfield from those of the uncharged species (Figure 1). The signals of the α-protons shift less, by a factor of one-half, compared to those of the β-protons. This cannot be explained in terms of electron density alone.[9-11] In the case of most com-

TABLE 4

Hammett σ constants and differences in $\mathrm{p}K_\mathrm{a}$ values

| Substituent | σ [a] | $\Delta\mathrm{p}K_\mathrm{a}$ [b] | $\Delta\mathrm{p}K_\mathrm{a}$ [c] |
|---|---|---|---|
| 4-Ac | 0·52 | 1·77 | 1·69 |
| 3-Ac | 0·31 | 2·14 | 2·05 |
| 4-NH$_2$ | −0·66 | −3·84 | −4·37 |
| 4-Br | 0·23 | 1·39 | 1·26 |
| 4-Cl | 0·23 | 1·26 | 1·16 |
| 3-Cl | 0·37 | 2·49 | 2·43 |
| 4-CN | 0·63 | 3·21 | 3·05 |
| 3-CN | 0·68 | 3·79 | 3·72 |
| 4-NH$_2$ | −0·83 | −4·39 | −4·16 |
| 4-CO$_2$H | 0·27 | 0·75 | 0·60 |
| 2,4-Me$_2$ | −0·22 | −1·86 | −1·37 |
| 2,5-Me$_2$ | −0·12 | −0·83 | −0·94 |
| 2,6-Me$_2$ | −0·10 | −1·32 | −1·50 |
| 3,4-Me$_2$ | −0·24 | −0·93 | −0·92 |
| 3,5-Me$_2$ | −0·14 | −0·50 | −0·72 |
| 4-SH | 1·60 | 3·70 | 3·75 |
| 4-CH$_2$NH$_2$ | | 0·93 | 0·90 |
| 3-CO$_2$H | 0·36 | 1·16 | 1·33 |
| 2-Me | −0·05 | −0·30 | −0·60 |
| 3-Me | −0·07 | −0·17 | −0·37 |
| 4-Me | −0·17 | −0·55 | −0·73 |
| 4-CHO | 0·22 | 0·63 | 0·45 |
| H | 0·00 | 0·00 | 0·00 |

[a] For distributed compounds σ is the sum of the individual σ's for each substituent. [b] Calculated relative to the $\mathrm{p}K_\mathrm{a}$ for pyridine at 37 °C. [c] Calculated from the extrapolated $\mathrm{p}K_\mathrm{a}$ values for the substituted pyridines at 25 °C relative to the extrapolated value obtained for the $\mathrm{p}K_\mathrm{a}$ of pyridine at 25 °C.

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[7] H. C. Brown, D. H. McDaniel, and O. Haffinger, in E. A. Braude and F. C. Nachod, ' Determination of Organic Structures by Physical Methods,' Academic Press, New York, 1955.

[8] D. D. Perrin, ' Dissociation Constants of Organic Bases in Aqueous Solutions,' Butterworth, London, 1965.

[9] M. R. Chakrabarty and J. L. Roberts, unpublished work.

[10] V. M. S. Gill and J. N. Murrell, *Trans. Faraday Soc.*, 1964, **60**, 248.

[11] J. D. Baldeschwieler and E. W. Randall, *Proc. Chem. Soc.*, 1961, 303.

pounds, this shift from the charged to the uncharged species is *ca.* 20 Hz for the α-protons and 40 Hz for the β-protons (Table 1). The major exceptions were the two 4-nitrogen substituted pyridines, 4-amino- and 4-dimethylamino-pyridine. In these, the value of Δν for both the α- and β-positions was about one-half that observed for the other compounds. This cannot be explained by tautomerization involving the 4-nitrogen atom since the 4-mercapto-compound does not show this unusually small value of Δν. The resolution of the α-protons is greatly affected in the intermediate range between completely protonated and unprotonated forms. The resolution of the β-protons on the other hand increases markedly upon deprotonation. Figure 1 illustrates this for the case of pyridine.

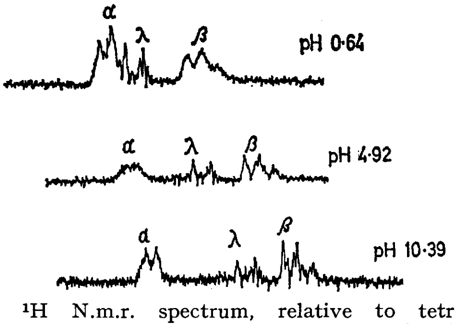


FIGURE 1 $^1$H N.m.r. spectrum, relative to tetramethylammonium chloride, of pyridine in acid and basic solutions at 70 ± 2 °C

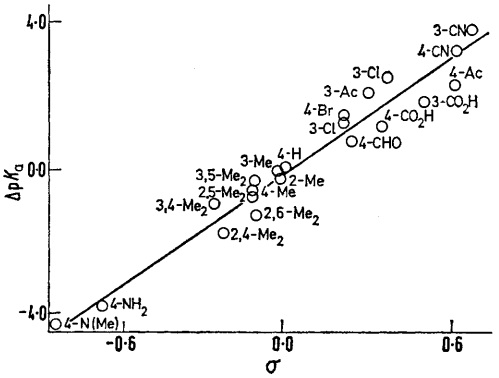


FIGURE 2 Hammett plot of $\Delta pK_a$ of substituted pyridines using the values at 37 °C. The equation for the computer-generated least-squares line is $5{\cdot}35 - 5{\cdot}23\Sigma\sigma$. Standard deviation 0·26, correlation coefficient 0·975

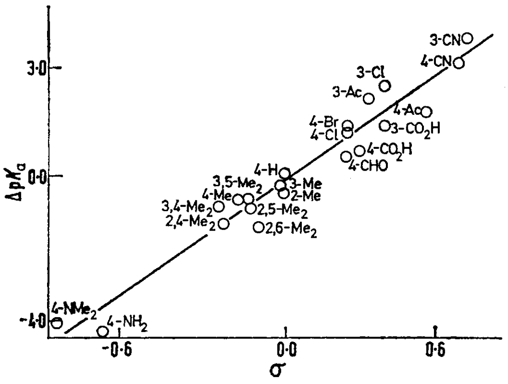
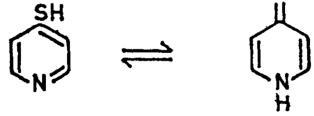


FIGURE 3 Hammett plot of $\Delta pK_a$ of substituted pyridines using the values at 25 °C. The equation for the computer-generated, least-squares line is $5{\cdot}31 - 5{\cdot}13\Sigma\sigma$. Standard deviation 0·30, correlation coefficient 0·968.

Thermodynamic values for ionization of only a few of these pyridines have been reported previously.[2,8,12] Our data are in good agreement with those reported by Essery and Schofield.[12] The introduction of an electron-releasing group increases the value of $pK_a$ while electron-withdrawing groups decrease it. This can be seen from plots of $\Delta pK_a$ *vs.* the Hammett σ constants[13] of the substituent groups (Figures 2 and 3). The value of the $\Delta pK_a$ of 4-mercaptopyridine is much lower than expected from σ. This can be explained along the lines reported by Katritzky.[14] For this compound, the thione predominates. For SH a more reasonable value for σ, especially when applied to heterocyclic systems, is +0·73 instead of 1·60. Katritzky reports that this equilibrium is more important for aminopyridines than for mercaptopyridines. This equilibrium constant in favour of the thione has been reported to be $10^{4\cdot5}$.[14] This seems, however, not to be the case since the $pK_a$ values of 4-amino- and 4-dimethylamino-pyridine lie close to the least-squares line. The correlation coefficient of the line is 0·975.



(4)

The $pK_a$ value for 2,6-dimethylpyridine is slightly off the line. In this case, the increased acidity of the pyridinium ion is due to steric effects imposed by the α-substituents. The results of this plot also indicate the σ value for the 4-aminomethyl group on pyridine to be 0·20. The slope indicates that the $pK_a$ of a substituted pyridine could be estimated at 37 °C by equation (5).

$$pK_a = 5{\cdot}35 - 5{\cdot}23\Sigma\sigma \qquad (5)$$

The current interest in biological systems where heterocyclic bases are known to play important roles makes determination of ionization constants and thermodynamic properties useful. Other than extrapolated values, little if any information exists on these data at 37 °C. It is important to have complete data for biologically useful heterocyclic bases directly measured at temperatures encountered in living systems. The results here illustrate the behaviour of a simple model system at this temperature.

Equation (6) from the extrapolated $pK_a$ values allows the estimation of ionization constants for substituted pyridinium ions at 25 °C. The correlation coefficient for this equation

$$pK_{a(25\,°C)} = 5{\cdot}31 - 5{\cdot}13\Sigma\sigma \qquad (6)$$

is 0·966. Several earlier workers have obtained similar equations.[15,16] Vaughan and his co-workers[15] reported the equation as $5{\cdot}21 - 6{\cdot}01\Sigma\sigma$, using $\sigma^0$ constants. σ Values

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[12] J. M. Essery and K. Schofield, *J. Chem. Soc.*, 1961, 3939.

[13] Values for σ constants are from either Y. Okamoto, T. Inukai, and H. C. Brown, *J. Amer. Chem. Soc.*, 1958, **80**, 4979, or H. H. Jaffé, *Chem. Rev.*, 1953, **53**, 191. Values for $\sigma^0$ constants are from R. W. Taft, jun., S. Ehrenson, I. C. Lewis, and R. E. Glick, *J. Amer. Chem. Soc.*, 1959, **81**, 5352.

[14] R. A. Y. Jones, and A. R. Katritzky, *J. Chem. Soc.*, 1958, 3610.

[15] A. Fischer, W. J. Galloway, and J. Vaughan, *J. Chem. Soc.*, 1964, 3591.

[16] H. H. Jaffé and G. O. Doak, *J. Amer. Chem. Soc.*, 1955, **77**, 4441.

give better results than $\sigma^0$ values, since these constants also include a resonance contribution. In our study, as in Jaffé's, there is interaction of the non-bonding electrons with the $\pi$ system of the ring for most substituents.

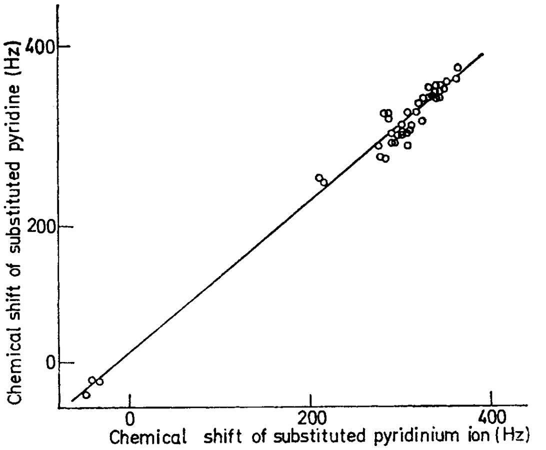

FIGURE 4 $^1$H N.m.r. chemical shifts of monosubstituted pyridines *vs.* the chemical shifts of the corresponding pyridinium ions. Shifts are relative to tetramethylammonium chloride.

A plot of $\nu_B$ *vs.* $\nu_{BH^+}$ for the monosubstituted pyridines resulted in a straight line (Figure 4), $\nu_B = 0{\cdot}98\ \nu_{BH^+} - 22{\cdot}6$ with correlation coefficient 0·987. An equation for a similar plot of chemical shifts of the acidic and basic forms of methyl substituted pyridines, $\nu_B = 0{\cdot}90\ \nu_{BH^+} - 22{\cdot}3$, has been reported.[2] Thus, protonation affects the chemical shift in all of these compounds in a similar manner. Similarly, a plot of $\Delta H$ *vs.* p$K_a$ (Figure 5) is a straight line indicating that solvation effects for the compounds studied are similar. For the methyl substituted pyridines $\Delta H$ (in kcal) is related to p$K_a$ by equation (7). This equation

$$\Delta H = 1{\cdot}41\text{p}K_a - 2{\cdot}34 \qquad (7)$$

compares well with that reported by Sacconi and his coworkers[17], $\Delta H = 1{\cdot}49\text{p}K_a - 2{\cdot}89$. From our data, the relationship for all substituted pyridines is given by equation (8).

$$\Delta H = 1{\cdot}78\text{p}K_a - 4{\cdot}59 \qquad (8)$$

Linear dependence of p$K_a$, and hence $\Delta G$, on $\Delta H$ would not be expected to occur in all cases, since the latter comprises contributions from both $\Delta H$ and $\Delta S$. However, in cases of compounds closely resembling one another electronically, as well as sterically, one may expect such a trend. In general, in the case of substituted pyridines reported here, this seems to be the case.

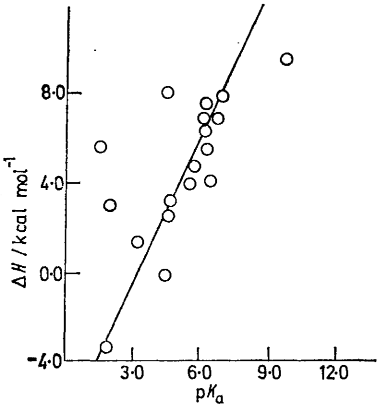

FIGURE 5 Plot of $\Delta H$ for the substituted pyridines *vs.* their p$K_a$ values at 25 °C

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[17] L. Sacconi, P. Paoletti, and M. Ciampolini, *J. Amer. Chem. Soc.*, 1960, **82**, 3831.