Linear Free Energy Relationships. Part VI.[1] Acidity of 4-(5-X-2-Hydroxystyryl)-*N*-methylpyridinium Iodides

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The pK_a values of the title compounds have been determined spectrophotometrically as a function of temperature in a number of buffer systems. In all cases pK_a is a linear function of substituent constant, σ_x, and ranges from 5.8 to 8.7 at room temperature. From the pK_a values of 4-(2-hydroxystyryl)-*N*-methylpyridinium iodide and the corresponding *N*-benzyl compound apparent *ortho* substituent constants, σ^-_{ortho}, for the 4-vinyl-*N*-alkylpyridinium groups were assigned (+0.61 ± 0.04 and +0.70 ± 0.01, respectively) and compared to the *para*-substituent constant (+0.61 ± 0.02) for the 4-vinyl-*N*-methylpyridinium group evaluated from published data. Differences between thermodynamic parameters (ΔH° and ΔS°) in borate-containing buffers and those in other buffers are attributed to specific interaction with boric acid. All the results are consistent with a significant contribution from quinonoid forms involving the pyridyl ring to the ground states for these compounds and their solvatochromic conjugate bases in aqueous solution; however, this contribution increases upon excitation.

SOLVATOCHROMIC compounds change colour (absorption spectrum) with solvents.[2,3] They are of interest from a number of viewpoints. Our past efforts with solvatochromic compounds [4,5] were designed to learn more about the ability of Hammett-type substituent constants (σ) to correlate molecular orbital energy levels as part of a program on linear free energy relationships.[1,6,7] In our previous work using series (1)—(4) the long wavelength $\pi\rightarrow\pi^*$ transitions were shown to be due to an intramolecular charge transfer from the phenol or phenolate system to the pyridyl or pyridinium groups. In effect then electron density is shifted from the highest occupied molecular orbital (HOMO) of the phenol–quinone system

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[1] Part V, H. W. Gibson, *J. Amer. Chem. Soc.*, 1975, **97**, 3832.

[2] W. Liptay, *Angew. Chem. Internat. Edn.*, 1969, **8**, 177.

[3] C. Reichardt, *Angew. Chem. Internat. Edn.*, 1965, **4**, 29.

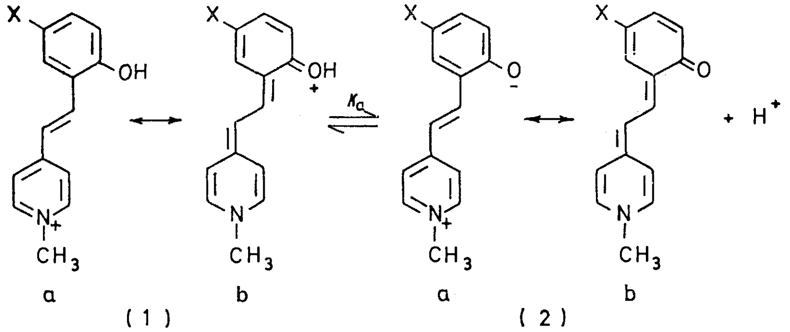
[4] H. W. Gibson and F. C. Bailey, *Tetrahedron*, 1974, **30**, 2043.

[5] H. W. Gibson and F. C. Bailey, *Canad. J. Chem.*, 1975, **53**, 2162.

[6] H. W. Gibson, *Canad. J. Chem.*, 1973, **51**, 3065.

[7] J. E. Kuder, H. W. Gibson, and D. Wychick, *J. Org. Chem.*, 1975, **40**, 875.

to the lowest unoccupied molecular orbital (LUMO) associated with the pyridyl–pyridinium portion. Attachment of substituents to the phenol–quinone group is primarily expected to alter the energy of the HOMO in series (1) and (2) since they are *meta* to the styrylpyridinium group, while the LUMO of the pyridyl–pyridinium ring responds more strongly to substituents in (3) and (4). As expected on the basis of previous work with ionization potentials [6] and electron affinities,[8] the HOMO energy decreases with increasing σ, raising the transition energies of (1) and (2),[4] and the LUMO energy decreases with increasing σ, lowering the transition energies of (3) and (4).[5] Thus, in the previous work the electron distributions between (1)—(4) and their excited states were qualitatively deduced. In each case the contribution of resonance form b to the ground state is less than to the excited state or conversely the relative importance of resonance form a is greater in the ground state than in the excited state.



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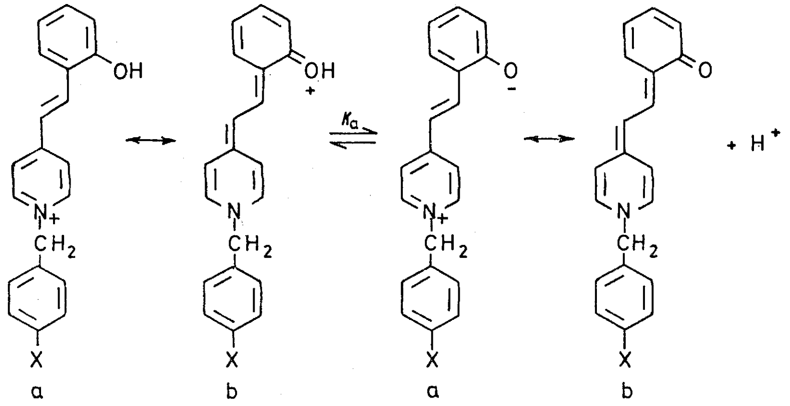


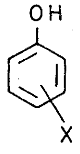
(3) (4)

Another useful technique for learning the relative electron distribution of a molecule or the effect of substituents on a series of molecules is to examine the acidity.[9] This report is a description of the determination of the acid–base properties of series (1) in the ground state.

The acidity of a number of families of phenols have been studied. For a series of *meta*- and *para*-substituted phenols (5) in water a linear relationship between $\mathrm{p}K_a$ and substituent constant was found [equation (1)].[10]

$$\mathrm{p}K_a = -2.23\sigma + 9.92 \qquad (1)$$

Earlier workers studied 13 phenols of structure (5) [11] with similar results.[12] Russian workers studied a series of 23 *ortho*-, *meta*-, and *para*-compounds in dimethyl sulphoxide at 25° and obtained an equation like (1) but with slope −2.7.[13] Similarly the $\mathrm{p}K_a$ values of the 4-substituted 2-nitrophenols (6) are correlated by the substituent constants with a slope of −2.16.[14] Later work using the



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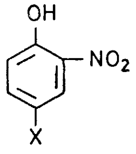

(6)

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[8] M. E. Peover, *Trans. Faraday Soc.*, 1962, **58**, 1656, 2370; P. Zuman, 'Substituent Effects in Organic Polarography,' Plenum Press, New York, 1967.

[9] K. B. Wiberg, 'Physical Organic Chemistry,' Wiley, New York, 1964, pp. 278—291.

[10] A. I. Biggs and R. A. Robinson, *J. Chem. Soc.*, 1961, 388.

[11] G. Kortüm, W. Vogel, and K. Andrussow, *Pure Appl. Chem.*, 1961, **1**, 190.

[12] H. H. Jaffé, *Chem. Rev.*, 1953, **53**, 222.

[13] A. P. Kreshkov, N. S. Aldarova, A. I. Tarasov, V. A. Vasner, S. V. Vinogradova, M. V. Slavgorodskaya, M. V. Mitaishvili, and V. V. Kovshak, *Reakts. spos. org. Soedinenii*, 1970, **7**, 279 (*Chem. Abs.*, 1970, **73**, 124, 179s).

[14] M. Rapoport, C. K. Hancock, and E. A. Meyers, *J. Amer. Chem. Soc.*, 1961. **83**, 3489.

results for 86 mono-, di-, tri-, tetra-, and penta-substituted phenols led to equation (2) with an average deviation of 0.18 pK_a unit.[15]

$$\mathrm{p}K_a = 9.94 - 2.26\Sigma\sigma \qquad (2)$$

In general by use of equations (1) or (2) it is possible to assign apparent σ constants for *ortho*-substituents such as the nitro-group of (6) and a variety of these have been compiled.[15,16] They then allow the prediction of pK_a values of multisubstituted phenols with reasonable accuracy (±0.2 usually).[15,16]

RESULTS AND DISCUSSION

Spectroscopic Characterization.—The pK_a values of (1; X = NO_2, Cl, H, or OCH_3) were evaluated at several temperatures spectroscopically by means of the characteristic long wavelength absorptions of (1) and the corresponding ' anions ' (2), which are given in Tables 1 and 2, respectively. Spectra of compounds (1 and 2; X = H) are displayed in Figures 1 and 2, respectively. As can be seen a significant change in the spectrum occurs on conversion into the solvatochromic form.

TABLE 1

Long wavelength absorption maxima of pyridinium Iodides (1) in aqueous solutions of pH 3.243 (at 22.2°)

	$\lambda_{max.}$/nm (±0.5)			
X	0°	22.2°	40.0°	69.6°
NO_2	347	347	343	341
Cl	372	371	372	368
H	367	366	362	363
OCH_3	392	388	387	384

TABLE 2

Long wavelength absorption maxima of betaines (2) in aqueous solutions of pH 10.484 (at 22.2°)

	$\lambda_{max.}$/nm (±0.5)			
X	0°	22.2°	40.0°	69.6°
NO_2	434	437	442	444
Cl	453	456	457	458
H	447	449	452	453
OCH_3	479	482	482	

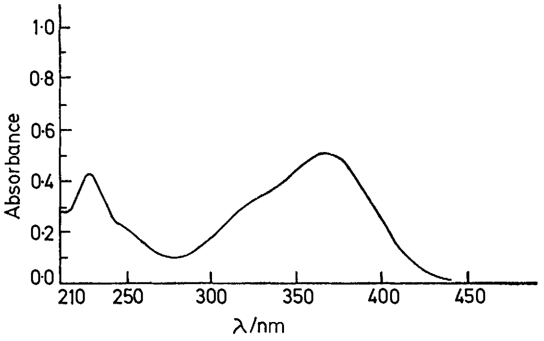

FIGURE 1 U.v.-visible spectrum of 1.06×10^{-5}M-iodide (1; X = H) in H_2O (borate–phosphate–acetate buffer; pH 3.243; 2 cm cells)

The evaluation of the pK_a values was accomplished by analysing a series of buffer systems for concentrations of the salt [(1)] and the solvatochromic form [(2)] using the absorptions, A, and the extinction coefficients, ε, evaluated at each temperature: $[(1)] = A_{(1)}/\varepsilon_{(1)}b$ (b = cell path in cm) and $[(2)] = A_{(2)}/\varepsilon_{(2)}b$. The p$K_a$ was calculated from equation (3).

$$\mathrm{p}K_a = \mathrm{pH} - \log(A_{(1)}\varepsilon_{(2)}/A_{(2)}\varepsilon_{(1)}) \qquad (3)$$

Our original determinations used borate–phosphate–acetate buffers, but electrochemical studies indicated some interaction of borate ion or boric acid with species (1) and/or (2).[17] Therefore the acidity of series (1) was also examined in three other buffer systems: citrate, phosphate, and tris(hydroxymethyl)aminomethane. Each member of series (1) was examined in all three buffers at at least one temperature in order to distinguish any specific interactions. The positions of the absorption maxima are insensitive to these buffers. The extinction coefficients obtained for species (1) and (2) at the extremes of pH in non-borate and borate buffers do vary (see below).

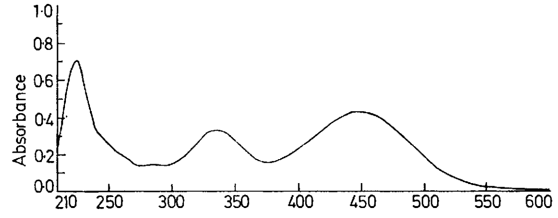

FIGURE 2 U.v.-visible spectrum of 1.06×10^{-5}M-betaine (2; X = H) in H_2O (borate–phosphate–acetate buffer; pH 10.484; 2 cm cells)

Temperature Effects on Long Wavelength Absorption Maximum.—Examination of Tables 1 and 2 reveals trends in the long wavelength absorption maxima ($\lambda_{max.}$) as functions of temperature. In each case the $\lambda_{max.}$ of the solvatochromic forms (2) increases with increasing temperature, while $\lambda_{max.}$ of the salts (1) decreases with increasing temperature.

The simplest explanation of these results is that the extent of hydrogen bonding, which effects the spectra, is temperature dependent in opposite directions for (1) and (2). An alternative way to rationalize these results involves the origin of the absorption band shape.[18]

If the Morse curves shift, the equilibrium separation distance difference, $r_e - r_g$, must decrease, thereby increasing the probability of the lower energy transitions. If the Morse curves do not shift, the vibrational energy level spacings of the excited state must decrease relative to those of the ground state, thereby lowering the energy of all the transitions. In the case of salts (1) population of higher vibrational levels at higher temperature can be excluded as an explanation for the temperature effect

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[15] P. J. Pearce and R. J. J. Simkins, *Canad. J. Chem.*, 1968, **46**, 241.

[16] G. R. Barlin and D. D. Perrin, *Quart. Rev.*, 1966, **20**, 75.

[17] P. Zuman, personal communication.

[18] For a full discussion, see G. M. Barrow, ' Molecular Spectroscopy,' McGraw-Hill, New York, 1962, ch. 10, 11; H. H. Jaffé and M. Orchin, ' Theory and Applications of Ultraviolet Spectroscopy,' Wiley, New York, 1966, pp. 134—145.

since it is in the opposite direction. If the relative positions of the Morse curves change, then $r_e - r_g$ must increase. If the relative vibrational spacings are effected those of the excited state must increase relative to those of the ground state.

Temperature and Buffer Effects on Extinction Coefficient.—The extinction coefficients were found to be a function of the buffer system employed. The results at 0° will be used for comparison. The values for the salts (1; X = Cl, H, or OCH_3) are 25—29% lower in citric acid–sodium citrate (pH 3.544 at 23.0°) than in the acetate–borate–phosphate system (pH 3.243 at 23.0°) while ε for (1; X = NO_2) is 17% higher in the citrate system. The results for solvatochromic betaines (2) are similar; ε values for (2; X = Cl, H, or OCH_3) are 3—11% lower in sodium hydroxide–sodium carbonate (pH 10.484 at 23.0°) than in the acetate–borate–phosphate system (pH 10.484 at 22.2°) while ε for (1; X = NO_2) is 11% higher in the citrate. Thus in both (1) and (2) the nitro-compound is anomalous. There are several explanations for the dependence of ε on buffer system. First, the extent of hydrogen bonding could vary with solvent composition. A closely related possibility is that complexation occurs in one or more of the buffers; in fact, other results (see below) suggest that boric acid or borate ion does complex with either or both (1) and (2). Either of these contingencies would be expected to alter the extinction coefficient.

We turn now to the temperature dependences. It was found that the extinction coefficients vary by up to 14% over the temperature range 0—69.6°. No patterns emerge from these temperature dependences, which can be ascribed to temperature dependent solvent effects (hydrogen bonding, complexation) or changes in Morse curves.[18]

Chemical Stability of Compounds in Solution.—The stability of each of the compound–buffer solution combinations used in this work was checked by examining freshly prepared solutions and then aged solutions and solutions before and after heating. A number of pertinent observations were made.

In both borate and non-borate buffers (1; X = OCH_3) was found to be unstable at 70°. Moreover, even at room temperature decomposition occurs over a period of a few days. The remaining members of series (1) were relatively stable in the borate-containing buffers, but did seem to deteriorate to some extent as evidenced by decreases in the intensity of the bands from both (1) and (2) over a period of a few weeks. In the non-borate buffers, in acidic solution particularly, (1; X = Cl) underwent a rapid change. One might hazard the speculation that a small percentage of OH protonated (1; X = Cl) is present and that this undergoes nucleophilic attack by citrate, hydrogen citrate, or most likely at this pH, dihydrogen citrate anion, resulting in loss of Cl^-

In view of the instabilities noted here all spectral determinations were carried out with freshly prepared solutions. In the two cases noted above the samples were prepared minutes prior to the determination. In other cases most determinations were made within a few hours.

Acidities.—All pK_a results are summarized in Table 3. Examination of Table 3 reveals that agreement between results from the several non-borate buffers is excellent. The borate buffers appear to be different from the others, especially for (1; X = NO_2).

TABLE 3

pK_a of salts (1) as a function of temperature and buffer

X	T/°C	10^3T^{-1}/K^{-1}	Buffer system (n) [a]	pK_a (standard deviation)	
NO_2	0.0	3.660	B (3)	6.17 (0.04)	
			C (2)	6.08 (0.05)	6.04 (0.06)
			P (2)	6.00 (0.01)	
(σ_p 1.24)[10]	22.2	3.385	B (4)	5.74 (0.05)	
	23.0	3.376	C (2)	5.84 (0.01)	5.84 (0.01)
			P (2)	5.82 (0.01)	
	40.0	3.193	C (2)	5.66 (0.01)	5.65 (0.02)
			P (2)	5.63 (0.02)	
	69.6	2.917	B (3)	5.63 (0.02)	
	70.0	2.914	C (2)	5.32 (0.01)	5.33 (0.02)
			P (2)	5.33 (0.01)	
Cl	0.0	3.660	B (3)	8.11 (0.01)	
			P (3)	8.09 (0.02)	
(σ_p 0.23)[20]	22.2	3.385	B (5)	7.85 (0.02)	
	23.0	3.376	P (3)	7.91 (0.01)	7.92 (0.01)
			T (1)	7.93 (—)	
	40.0	3.193	P (3)	7.68 (0.01)	
	69.6	2.917	B (2)	7.57 (0.01)	
H	0.0	3.660	B (2)	8.62 (0.04)	
			T (4)	8.69 (0.02)	
(σ_p 0.00)[20]	22.2	3.385	B (5)	8.39 (0.04)	
	23.0	3.376	P (1)	8.50 (—)	8.49 (0.03)
			T (4)	8.49 (0.03)	
	40.0	3.193	P (1)	8.29 (—)	8.25 (0.03)
			T (3)	8.24 (0.01)	
	69.6	2.917	B (2)	8.13 (0.01)	
OCH_3	0.0	3.660	B (3)	8.92 (0.06)	
			T (3)	8.89 (0.02)	
(σ_p −0.11)[10]	22.2	3.385	B (4)	8.63 (0.02)	
	23.0	3.376	T (3)	8.68 (0.03)	
	40.0	3.193	B (3)	8.44 (0.03)	
			P (1)	8.40 (—)	8.40 (0.02)
			T (3)	8.41 (0.03)	

[a] B = Boric acid–phosphoric acid–acetic acid–sodium hydroxide; C = citric acid–sodium citrate; P = potassium dihydrogen phosphate–sodium hydroxide; T = tris(hydroxymethyl)aminomethane–hydrochloric acid; n = number of determinations.

Substituent Effects on Acidity.—The pK_a results were further analysed for substituent effects. Correlations between pK_a and the *para*-substituent constant, σ_{para}, for the non-borate and borate buffers are displayed graphically in Figures 3 and 4. Excellent correlations result in both borate and non-borate buffers at each temperature as evidenced by high correlation coefficients (r). The slopes, m, of these relationships range from −2.01 to −2.18. They are thus in general agreement with the average slope given in equations (1) and (2) for 25° and that (−2.16) of 4-substituted 2-nitrophenols (6).[14]

A more detailed look shows that for the borates the slope is a maximum at 22.2° while for the non-borate buffers the slopes decrease with increasing temperature. The borate slopes no doubt reflect the interaction of this buffer system with the compounds under study.

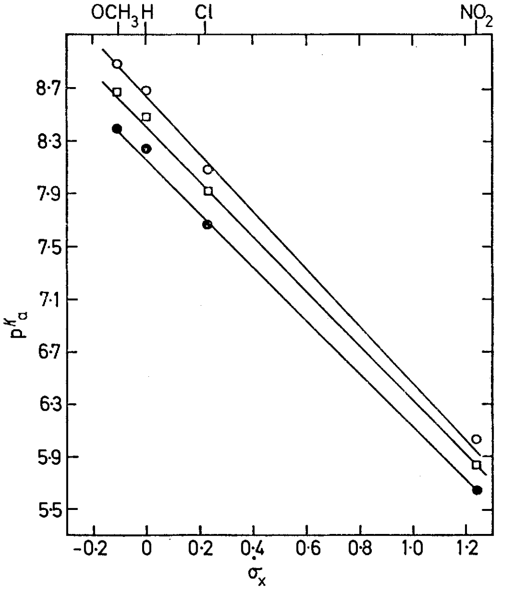


FIGURE 3 pK_a of 10^{-5}M-iodides (1) in non-borate buffers [citrate, phosphate, or (trishydroxymethyl)aminomethane not at constant ionic strength] *versus* the Hammett substituent constant, σ_{para}: ○, 0.0°, $pK_a = -2.18\sigma_{para} + 8.65$ (r 0.9971); □, 23.0°, $pK_a = -2.08\sigma_{para} + 8.41$ (r 0.9998); ●, 40.0°, $pK_a = -2.04\sigma_{para} + 8.16$ (r 0.9995)

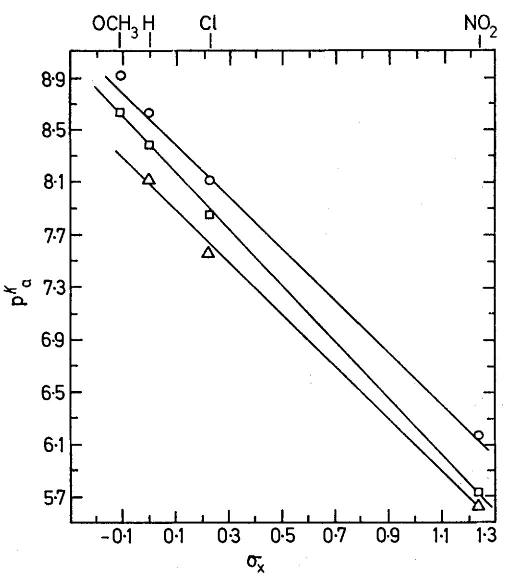
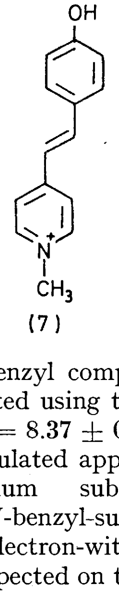


FIGURE 4 pK_a of 10^{-5}M-iodides (1) in borate buffers (phosphate–acetate–borate buffers not at constant ionic strength) *versus* the Hammett substituent constant, σ_{para}: ○, 0.0°, $pK_a = -1.96\sigma_{para} + 8.57$ (r 0.9985); □, 22.2°, $pK_a = -2.16\sigma_{para} + 8.38$ (r 0.9994); △, 69.6°, $pK_a = -2.01\sigma_{para} + 8.09$ (r 0.9979)

Using equation (2) and the present results at 23.0°, it is possible to assign an apparent σ^{-}_{ortho} constant to the 4-vinyl-*N*-methylpyridinium group; using the non-borate buffers an average value of +0.61 (±0.04) is obtained. Interestingly the σ^{-}_{para} value for this substituent calculated by equation (2) from the pK_a (8.57 at 27°, phosphate buffer) of 4-(4-hydroxystyryl)-*N*-methylpyridinium (7) iodide [19] is +0.61 (±0.02). The virtual identity of the values for the two positions suggests two things. (1) The 4-vinyl-*N*-methylpyridinium group in the *ortho*-position exerts very little effect on the acidity by a direct through space interaction (steric repulsion or hydrogen bonding) and (2) the group's influence is essentially by a resonance interaction, inductive effects being inconsequential. An alternative to these two deductions is that the additional electron-withdrawing inductive effect of the substituent in the *ortho*- relative to the *para*-position is just offset by a through space interaction.



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The acidity of *N*-benzyl compound (3; X = H) at 22.2° has been evaluated using the acetate–phosphate–borate buffers: pK_a = 8.37 ± 0.01.[5] From this and equation (2) the calculated apparent σ^{-}_{ortho} for the 4-vinyl-*N*-benzylpyridinium substituent is +0.70 (±0.01). Thus, the *N*-benzyl-substituted vinylpyridinium nucleus is more electron-withdrawing than the *N*-methyl. This is as expected on the basis of the substituent constants, σ_{para}, for benzyl and methyl (−0.09 and −0.17, respectively) [20] and phenyl and hydrogen (0.02 and 0.00, respectively).[20]

It is instructive to compare the σ^{-} values for the *N*-methyl and *N*-benzyl 4-vinylpyridinium substituents to the σ^{-}_{para} value of +0.619 reported for the styryl group.[21] The identity of σ for styryl and 4-vinyl-*N*-methylpyridinium and the closeness of that of the former to that of 4-vinyl-*N*-benzylpyridinium is somewhat surprising, inasmuch as the presence of a positive charge would be expected to cause an increase in electron-withdrawing power relative to the styryl group. Nonetheless these results reveal a substantial delocalization of the positive charge in the pyridinium ring of (1) and (3) and the conjugate bases (2) and (4) through contributions of quinonoid resonance forms (1b)—(4b). Thus, these results taken with our previous conclusion that the ground states of (1)—(4) possess more of the character of resonance forms a than the excited states [4, 5] means that the

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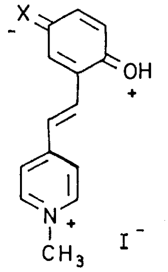
[19] J. E. Kuder and D. Wychick, *Chem. Phys. Letters*, 1974, **24**, 69.

[20] O. Exner in 'Advances in Linear Free Energy Relationships,' eds. N. B. Chapman and J. Shorter, Plenum Press, New York, 1972, pp. 28—29.

[21] H. H. Jaffé, *Chem. Rev.*, 1953, **53**, 191.

large contribution of forms b to the ground states are significantly increased upon excitation. This is in accord with Huckel molecular orbital calculations on (7).[19]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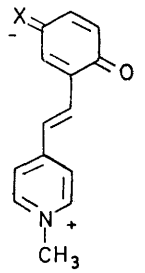
(9)

Thus, the ionization of phenols (1) and (3) is analogous to more simply substituted phenols such as (5) and (6). Additional quinonoid contribution to the ground state structures of (1) and (2) due to the effect of substituent X is indicated in (8) and (9). In fact (9; X = NO_2) was invoked as a contributor to the structure of (2; X = NO_2) in order to explain its relatively low solvatochromism.[4] That is, contribution of (9) decreases the importance of (2b) and hence also decreases the solvatochromism. This rationalization is borne out by the present results in the following manner. The σ^{-}_{ortho} values calculated for the 4-vinyl-*N*-methylpyridinium system is a measure of the contribution of (2b). For (2; X = OCH_3) a value of 0.67 results from equation (2), while for (2; X = NO_2) the value is 0.58. This translates to a 15% decrease in contribution of (2b) to the ground state by substitution of NO_2 for OCH_3. The greater importance of structure (2b) in the excited state is reflected by the fact that the solvatochromism decrease is 30%.

Temperature Effects on Acidity.—The data of Table 3 were also analysed for temperature effects. Figure 5 contains a van't Hoff plot for each member of series (1) in non-borate buffers. The linear least squares correlations are summarized in Table 4, as are the thermodynamic parameters derived therefrom: the standard enthalpy change $\Delta H°$, the standard free energy change $\Delta G°_{298}$, and the standard entropy change $\Delta S°_{298}$.

The van't Hoff plot for the borate-containing buffers is also given in Figure 5 and the thermodynamic parameters are listed in Table 5. As can be seen from Figure 5 the van't Hoff plot for (1; X = NO_2) is non-linear in borate buffers. Thus, $\Delta H°$ is not constant over the temperature interval and no attempt was made to evaluate the thermodynamic parameters. For the other three members of series (1) very good to excellent correlations result.

Comparison of Tables 4 and 5 reveals a striking difference in the calculated $\Delta H°$ values in borate *versus* non-borate buffers for (1; X = Cl and H). The values are *ca.* 1.2 kcal mol^{-1} higher in the non-borate buffer. The values for (1; X = OCH_3) are virtually identical. The values for $\Delta G°_{298}$ and $\Delta S°_{298}$ are within the standard deviations for X = H and OCH_3 and just outside this range for the $\Delta S°_{298}$ for X = Cl. The implication for these results is the same as that gained from examination of the data in Table 3, namely that the pK_a values at a given temperature for (1; X = Cl or H) are very close for borate and non-borate buffers but that a different temperature dependence exists. This is the result of significant differences in $\Delta H°$. $\Delta S°$ Values do not reflect this because of the larger uncertainties in their calculation. Values for (1; X = OCH_3) are virtually identical. The curvature of the van't Hoff plot for (1; X = NO_2) in borate buffers and the linearity of this plot for non-borate buffers (Figure 5) are interpreted as being due to a distinctly temperature dependent interaction in the former case. Thus the effect on $\Delta H°$ of changing from non-borate to borate-containing systems is in the order $NO_2 > Cl > H > OCH_3$. This is the order of acidity and thus the evaluations of this series were in buffer solutions of increasing pH. It is thus tempting to ascribe the interaction to boric acid itself inasmuch as its concentration would be highest for evaluation of (1; X = NO_2)

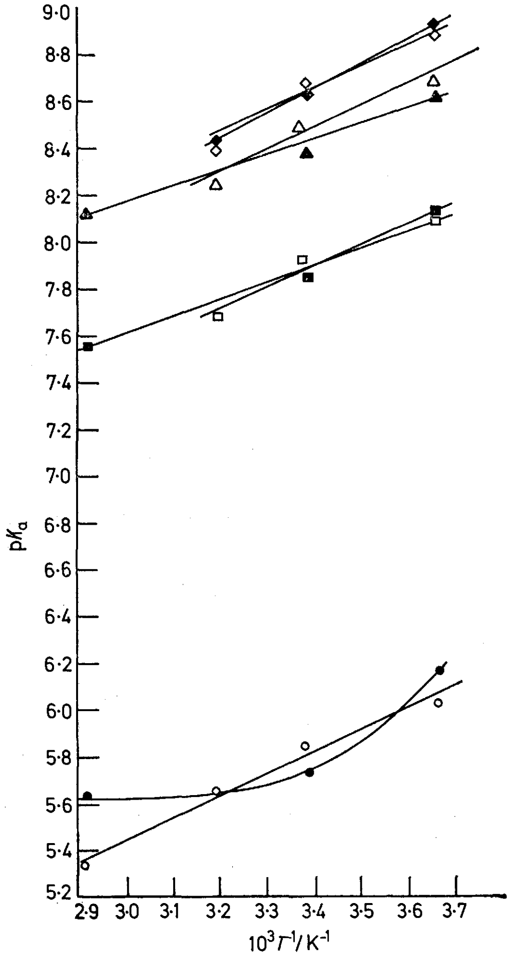

FIGURE 5 pK_a of 10^{-5}M-iodides (1) in borate and non-borate buffers *versus* reciprocal of absolute temperature (van't Hoff plot): ◊, X = OCH_3; △, X = H; □, X = Cl; ○, X = NO_2: open symbols, citrate, phosphate, or tris(hydroxymethyl)-aminomethane; closed symbols, acetate–borate–phosphate buffers

(buffers of pH *ca.* 5.7) and lowest for (1; X = OCH_3) (buffers of pH *ca.* 8.6). Such an interaction could occur between the phenolate and boric acid to give a Lewis acid–base complex similar to other known boron–oxygen complexes [ArO $B(OH)^-{}_3$].

The thermodynamic parameters for (7) in borate buffers are ΔH° 3.74 ±0.24 kcal mol^{-1}, ΔG°_{298} 11.7 ± 0.5 kcal mol^{-1}, ΔS°_{298} 26.8 ± 2.4 cal mol^{-1} K^{-1}.[19] Comparison of these results to those for (1; X = H) is informative. The ΔH° values for (7) lies between the values for borate (3.01 ± 0.07 kcal mol^{-1}) and non-borate (4.11 ± 0.34 kcal mol^{-1}) systems. However, taking the standard deviations into account the non-borate value of (1; X = H) overlaps that of (7). Since (7) was examined in a borate-containing buffer, this suggests that its ' anion ' does not specifically interact with borate while the isomeric (2; X = H) does, or alternatively that both do but only (2) is affected. This would not be the case were the above complex involved; both the ' anions ' of (2; X = H) and (7) should form such a complex. Boric acid does form chelate-type complexes with 2-hydroxy-carbonyl compounds.[22] Borates are known to interact with C=C double bonds also.[23] These facts in combination then suggest that a chelate-type complex of boric acid with the phenolate functions and the styryl double bond is responsible for the anomalous results with (2; X = H). For the conjugate base of (7) such a complex is not possible.

ΔG°_{298} and ΔS°_{298} are identical for (7) and (1; X = H) within the standard deviations, though the uncertainties as stated above are large. This apparent agreement of ΔS°_{298} is somewhat surprising. We had considered the possibility of intermolecular interaction of the hydroxy-group of (1) or the phenolate anion of (2) with the ethylene linkage and such an interaction should cause a change in ΔS°_{298} relative to (7), where such interactions are not possible. The present data, therefore, suggest that such interactions are not significant.

TABLE 4

Thermodynamic data from least squares fits of pK_a *versus* $1/T$ for non-borate buffers [a]

p$K_a = m\ (1/T) + b$

X	Slope 10^{-2} *m*	*r*	ΔH°/kcal mol^{-1}	ΔG°_{298}/kcal mol^{-1}	ΔS°_{298}/cal mol^{-1} K^{-1}
NO_2	10.7 ± 0.4	0.9969	4.92 ± 0.21	7.93 ± 0.41	−10.1 ± 2.1
Cl	9.77 ± 0.46	0.9702	4.47 ± 0.21	10.7 ± 0.4	−21.0 ± 2.0
H	8.99 ± 0.74	0.9884	4.11 ± 0.34	11.5 ± 0.7	−24.8 ± 3.5
OCH_3	10.4 ± 0.6	0.9883	4.74 ± 0.28	11.7 ± 0.6	−23.4 ± 3.0

[a] Least squares fit takes standard deviation of estimated pK_a values into account. The ± values reflect only the standard deviations of the slopes, *m*. They are not error estimates.

TABLE 5

Thermodynamic data from least squares fits of pK_a *versus* $1/T$ for borate-containing buffers [a]

p$K_a = m\ (1/T) + b$

X	Slope 10^{-2} *m*	*r*	ΔH°/kcal mol^{-1}	ΔG°_{298}/kcal mol^{-1}	ΔS°_{298}/cal mol^{-1} K^{-1}
Cl	7.22 ± 0.19	0.9973	3.30 ± 0.09	10.7 ± 0.2	−24.8 ± 1.0
H	6.57 ± 0.15	0.9996	3.01 ± 0.07	11.5 ± 0.1	−28.5 ± 0.6
OCH_3	10.2 ± 0.13	0.9997	4.65 ± 0.06	11.7 ± 0.1	−23.7 ± 0.6

[a] Least squares fit takes standard deviation of estimated pK_a values into account. The ± values reflect only the standard deviations of the slopes, *m* and are not error estimates.

Comparison of the present thermodynamic parameters with those of other phenols is also enlightening. In aqueous solutions ΔH° for 55 phenols ranges from 3.75 to 6.60 kcal mol^{-1} and ΔS°_{298} from −16.8 to −31.6 cal mol^{-1} K^{-1}.[24] Based on the ΔH° values the results in borate-containing buffers (Table 5; ΔH° 3.0—4.65 kcal mol^{-1}) definitely seem anomalous, while those in non-borate systems (Table 4; ΔH° 4.1—4.9 kcal mol^{-1}) are within the usual range. The ΔS° values for (1, X = Cl, H, or OCH_3) in both the borate-containing (−23.7 to −28.5 cal mol^{-1} K^{-1}) and non-borate systems (−21.0 to −24.8 cal mol^{-1} K^{-1}) are also not anomalous. ΔS°_{298} for (1; X = NO_2) (−10.0 cal mol^{-1} K^{-1}) in the non-borates is significantly outside the reported range for phenols. From the available data,[24] however, nitro-groups do appear to cause low ΔS° values as do formyl groups. Thus electron-withdrawing groups tend to lower ΔS°_{298}. As shown above the apparent *ortho*-substituent constant, σ^-_{ortho}, for the 4-vinyl-*N*-methylpyridinium substituent is +0.61 and thus it is a relatively strong electron withdrawer. It has been concluded that the changes in entropy relative to the unsubstituted compound (X = H) are due to differences in solvation.[25] The greater the charge delocalization, the lower the localized negative charge density on the phenolate oxygen and the lower the entropy of solvation. The ΔS°_{298} in such a case reflects a smaller change in solvation upon ionization. In the case of X = NO_2 the salt form (1) is quite polar due to the strongly electron-withdrawing character of the nitro-group [see (8)]. The resultant enchanced

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[22] J. Boeseken, *J. Phys. Chem.*, 1931, **35**, 1477; R. Brdicka, *Arkiv Kemi Mineral. Geol.*, 1948, **26B**, 7.

[23] W. J. Bover and P. Zuman, *J. Electrochem. Soc.*, 1975, **122**, 368; L. Deshler and P. Zuman, *Analyt. Chim. Acta*, 1974, **73**, 337.

[24] C. H. Rochester in ' The Chemistry of the Hydroxyl Group,' ed. S. Patai, Interscience, New York, 1971, pp. 374—375.

[25] L. P. Fernandez and L. G. Hepler, *J. Amer. Chem. Soc.*, 1959, **81**, 1783; C. L. Liotta, K. H. Leavell, and D. F. Smith, *J. Phys. Chem.*, 1967, **71**, 3091.

localized positive charges are more highly solvated which results in a higher $S°_{298}$ than for the other members of series (1) and the neutral phenols referred to above. In contrast, the negative charge of the phenolate portion of solvatochromic form (2) as represented by (2a) (see above) is more delocalized with $X = NO_2$ relative to X = Cl, H, or OCH_3 through contributions of (9), resulting in a lower $S°_{298}$ for (2; $X = NO_2$). The small $\Delta S°_{298}$ for $X = NO_2$ is thus a result of the relatively high $S°_{298}$ for (1) and the relatively low $S°_{298}$ for (2), compared with other members of the series. These results are also consistent with the conclusion reached above, namely that the ground state electron distributions of (1) and (2) are best represented by significant contributions from both a and b and also substituent (X) dependent contributions from quinonoid forms (8) and (9). On excitation, contributions from the quinonoid forms b increase relative to charge localized forms a.

EXPERIMENTAL

Buffer Solutions.—(a) *Acetic acid–boric acid–phosphoric acid–sodium hydroxide*. Following the reported procedure [26] buffer solutions of the following pH (22.2°) were prepared: 3.243, 4.942, 5.848, 6.380, 6.885, 7.565, 8.046, 8.293, 8.629, 8.866, 9.218, 9.437, 9.749, and 10.484.

(b) *Other buffers*. Buffers of pH (23.0°) 3.544, 5.270, and 5.770 were prepared from sodium citrate and citric acid.[27] From sodium hydroxide and potassium dihydrogen phosphate were prepared buffers [28] of pH (23.0°) 5.958, 6.417, 7.468, 7.852, and 8.052. Using hydrochloric acid and tris(hydroxymethyl)aminomethane, buffers [28] of pH (23.0°) 8.095, 8.317, 8.703, and 8.904 were prepared. A buffer of pH 10.484 was made from sodium hydroxide and sodium bicarbonate.[28]

pH *Determinations*.—A Beckman research pH meter was used to analyse the buffer solutions. The instrument was standardized using commercial reference buffers of pH 4.01 and 9.18 (22°). The pH of the appropriate solutions were measured at 0.0, 23.0, 40.0, 69.8, and 70.0° (after calibrating and standardizing at these temperatures) by use of a Lauda K-2/R constant temperature circulating system which controlled the temperature of a bath surrounding the sample to ±0.1°. The temperature of the sample was monitored with a chromel–alumel thermocouple and a Consolidated Controls Corporation digital indicator.

Spectral Determinations.—All spectral determinations were made on a Cary 15 spectrophotometer using 2.00 cm matched cells. For spectra at 0.0, 23.0, 40.0, 69.6, and 70.0° the sample cell was contained in a jacketted holder whose temperature was controlled by the circulating bath mentioned above. The cell temperature was monitored using the thermocouple and readout cited above. No volume corrections were applied.

pK_a *Determinations*.—Aqueous solutions of analytical samples [4] of the salts (1) were prepared at 10^{-4}M. These were diluted with buffer solutions to yield 10^{-5}M solutions. The extreme high and low pH solutions were then examined spectrally to determine the extinction coefficients of the salt (1) and solvatochromic form (2). The $\lambda_{max.}$ values of (1) and (2) are given in Tables 1 and 2. The spectra of (1 and 2; X = H) are given in Figures 1 and 2. The absorbances of the bands due to the salts (1) in buffer solutions of pH near the pK_a were corrected for the small contribution from the solvatochromic forms (2) in direct proportion to the $\lambda_{max.}$ absorbance of the bands due to the latter. Using these corrected absorbances, pK_a values were calculated using equation (3). The results are given in Table 3.

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[26] J. Heyrovsky and P. Zuman, 'Practical Polarography,' Academic Press, New York, 1968, p. 179.

[27] R. M. C. Dawson, D. C. Elliot, W. H. Elliot, and K. M. Jones, 'Data for Biochemical Research,' Clarendon Press, Oxford, 1959, p. 196.

[28] 'Handbook of Chemistry and Physics,' ed. R. C. Weast, CRC Press, Cleveland, 1974, p. D-113.