Consistency of the Indicator Overlap Method with Linear Free Energy–Enthalpy Correlations

P. D. Bolton,[1a] C. D. Johnson,[1b] A. R. Katritzky,[1b] and S. A. Shapiro[1b]

Contribution from the Wollongong University College,
University of New South Wales, Wollongong, N.S.W. 2500, Australia,
and the School of Chemical Sciences, University of East Anglia,
Norwich, England. *Received August 23, 1969*

Abstract: Previously established thermodynamic parameters for the ionization of weakly basic *p*-nitroanilines obtained by the overlap method have been shown to follow the same linear free-energy–enthalpy correlation governing ionization of strongly basic members of the series.

Arnett and Burke[2] have reported a precise linear relationship between the pK_a values of a series of substituted anilines (including most of the series now under discussion) and the partial molal heats of transfer of the compounds from *sym*-tetrachloroethane to 96.48% sulfuric acid. This was cited as evidence for the reliability of the Hammett overlap method,[3,4] which is the only means of determining the pK_a values in water of weak bases, and thus of establishing acidity functions in strongly acid media.

Table I. Thermodynamic Parameters for the Nitroanilines

Aniline	pK_{a25}, cal mol^{-1}	ΔG_{25}, cal mol^{-1}	ΔH_{25}, cal mol^{-1}	ΔS_{25}, cal deg mol^{-1}	ΔC_{p25}, cal deg mol^{-1}
4-Nitro	0.997 (0.003)[a]	1369 (2.0)	3085 (30)	5.8 (0.1)	
4-Nitro[b]	1.016 (0.001)	1390.5 (0.5)	3417 (18)	6.79 (0.06)	22 (3)
2-Nitro	−0.287 (0.024)	−429 (14)	1675 (217)	7.1 (0.7)	
2-Nitro[c]	−0.250 (0.001)	−336.9 (0.4)	1957 (11)	7.69 (0.04)	25 (1)
4-Chloro-2-nitro	−1.104 (0.028)	−1460 (17)	836 (255)	7.7 (0.9)	
2,5-Dichloro-4-nitro	−1.743 (0.036)	−2412 (22)	194 (328)	8.7 (1.1)	
2-Chloro-6-nitro	−2.414 (0.035)	−3267 (22)	−63 (325)	10.7 (1.1)	
2,6-Dichloro-4-nitro	−3.311 (0.025)	−4468 (15)	−1024 (228)	11.6 (0.8)	
2,4-Dinitro	−4.486 (0.041)	−5816 (25)	−3155 (378)	8.9 (1.3)	
2,6-Dinitro	−5.562 (0.036)	−7336 (22)	−4860 (333)	8.3 (1.1)	
2-Bromo-4,6-dinitro	−6.944 (0.046)	−9110 (28)	−6320 (424)	9.4 (1.4)	
3-Methyl-2,4,6-trinitro	−8.447 (0.26)	−11309 (161)	−7576 (2425)	12.5 (8.2)	
3-Bromo-2,4,6-trinitro	−9.518 (0.12)	−12808 (74)	−8113 (1118)	15.8 (3.8)	
2,4,6-Trinitro	−10.228 (0.12)	−13740 (76)	−9704 (1140)	13.5 (3.8)	

[a] The number in parentheses is the standard error of the measurement. [b] See ref 10a. [c] See ref 10b.

A recent publication from this laboratory[5] gave values for the H_0 acidity function measured over the temperature range 25–90°. An integral part of this work was the determination of the pK_a values of eleven substituted anilines by the overlap method with the measurements anchored on a determination of the thermodynamic pK_a value of 4-nitroaniline at the same temperature. From these temperature-variant pK_a values we have now calculated the thermodynamic functions of proton ionization by the nonempirical multiple equation method described by Clarke and Glew.[6] The considerable merit of this treatment over alternative approaches[7,8] lies in the fact that it neither presupposes a finite value of ΔC_p when the results are of insufficient accuracy to disclose one nor, when the results are sufficiently accurate, assumes any particular dependence of ΔH on temperature, other than, like ΔG and ΔS, it is a continuous well-behaved function of temperature.

It was found that in every case the simplest (straight line) relationship

$$R \ln K_a = \frac{-\Delta G^\circ_{25}}{298.15} + \frac{\Delta H_{25}}{298.15}\left(\frac{x}{1 + x}\right) \qquad (1)$$

where $x = (T - 298.15)/298.15$ gave the statistically

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(1) (a) Wollongong University College, University of New South Wales; (b) University of East Anglia.

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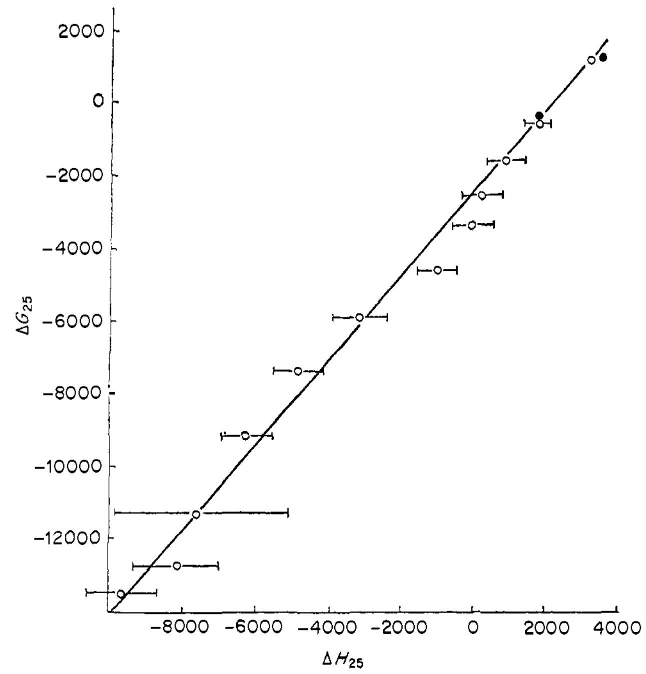

Figure 1. Linear free energy–enthalpy relationship for the dissociation of anilinium ions.

best representation of the above data. This is in keeping with the results of Bolton and Hall,[9,10] that ΔC_p for the proton ionization of many monosubstituted anilininium ions is small, the precision of the present results being insufficient to detect the small changes in enthalpy over the experimental temperature range. The results obtained are given in Table I.

The two strongest bases of the present work, 4-nitro- and 2-nitroaniline, have also been studied by Bolton and Hall,[10] and their results for these compounds are included in Table I. These latter results were obtained by spectrophotometric measurements in standard buffers or in aqueous hydrochloric acid solutions at a series of ionic strengths followed by extrapolation to zero ionic strength, at 5° temperature intervals over a 50° range. Allowing for the inevitably lower precision of the present work, the agreement must be considered encouraging.

Bolton and Hall[10] have also shown that sixteen out of the nineteen monosubstituted anilines studied gave a precise linear correlation between their thermodynamic pK_{a25} values and their enthalpies of proton ionization, ΔH_{25}, with only the three *o*-halogeno substituents deviating marginally from the line. The equation for the best straight line was

$$pK_a = 8.82\,(\pm 0.08) \times 10^{-4}\,\Delta H_{25} + 1.967\,(\pm 0.054) \quad (2)$$

Figure 1 shows that for the present series of anilines a similar linear correlation between pK_a (or ΔG) and ΔH exists. A determination of the best straight line through these points by weighted least-squares method[11] (*i.e.*, each point was given a weight inversely proportional to its standard error in ΔH_{25}) gave eq 3. Thus our results and those of Bolton and Hall lie on the same line, within error limits. The results overall thus

$$pK_a = 8.80(\pm 0.26) \times 10^{-4}\,\Delta H_{25} + 1.79(\pm 0.38) \quad (3)$$

constitute an example of a real linear enthalpy–entropy relationship,[12] the more meaningful graphical representation being ΔG *vs.* ΔH.[13]

While the precision of the overlap method clearly cannot match the accuracy of the standard spectrophotometric method, 2-nitroaniline is probably the weakest base which can be studied by the latter method. Extension of proton ionization studies to bases weaker than this must therefore inevitably involve the use of the overlap method. The present results thus reinforce the conclusions of Arnett and Burke[2] that such measurements can be undertaken with some confidence and pK_a values thus derived are of thermodynamic significance.

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