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THERMODYNAMIC FUNCTIONS OF PROTON IONISATION OF 1- AND 2-NAPHTHOL

P. De Maria and A. Fini*
Istituto di Chimica degli Intermedi, Universita' di Bologna, Viale Risorgimento 4, 40136 Bologna, Italy

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Abstract—Thermodynamic acidity constants of 1-naphthol have been measured spectrophotometrically over the temperature range 5–60° and those of 2-naphthol over the temperature range 5–50°. The thermodynamic functions of ionisation, ΔG°_{25}, ΔH°_{25}, ΔS°_{25} and ΔCp°_{25} have been calculated for both acids.

There have been many studies on the acidity of phenols in aqueous solution. These include not only measurements of pK_a,[1] but also enthalpies, entropies and heat capacities of ionisation.[2] Recently published pK_a values of 1- and 2-naphthol are available[3-5] at 25° as well as 21°. The strengths of naphthols can in general be predicted[1a] considering these acids as derived from phenol by annelation of a benzene ring, which has a specific σ constant of either 0.28 or 0.11 depending on whether the OH group is in position 1 or 2. However the thermodynamic functions of ionisation of naphthols do not seem to be known. Separation of the enthalpic and the entropic contribution to the free energy of ionisation often gives fundamental information on the effect of substituents on acidity[6] as well as on solute-solvent interactions.[2a] In this paper the thermodynamic functions of ionisation of titled compounds, ΔG°_{25}, ΔH°_{25}, ΔS°_{25} and ΔCp°_{25} have been calculated from thermodynamic acidity constant measured spectrophotometrically over a range of temperature in aqueous solution.

EXPERIMENTAL

Naphthols. Commercially available materials were carefully disublimed prior to use: m.ps and other physical properties were in agreement with literature values.

Dissociation constant determinations. In determining acid dissociation constants the simplest expression is given by (1) and the pK_a so calculated would be

$$pK_a = \text{"pH"} + \log_{10}[HA]/[A\ ] \qquad (1)$$

the concentration acidity constant. If "pH" in this expression is replaced by the thermodynamic acidity function value $p(a_H\,\gamma_{Cl})$,[7] then the thermodynamic acidity constant may be calculated from eqn (2)

$$pK_a = p(a_H\,\gamma_{Cl}) + \log_{10}(m_{HA}/m_{A^-}) \qquad (2)$$

provided that the initial concentration of the acid HA is sufficiently low to allow substitution of concentration terms for activities. The term m_{HA}/m_A is the ratio of acid to salt molalities in the buffer solution. This eqn (2) has been successfully used to determine thermodynamic pK_a values for a wide range of substituted phenols.[8,9] It has been shown that the experimental values so obtained are independent of the ionic strength of the solution, for solution of ionic strength < *ca.* 0.15. To confirm this finding, both naphthols were determined at different ionic strengths. The values obtained agree within experimental error and are reported in Table 1. In all cases the value of the ratio (m_{HA}/m_A) was determined for each temp. at three or more wavelengths close to the absorption maximum of base (A^-) form and the average value taken. The acidity function was corrected[10] for the small contribution arising from the ionisation of the naphthol. The absorbance by each soln, namely the buffer soln of the acid (HA and A), the fully protonated form (HA), and the fully deprotonated form (A) was corrected by also measuring the absorbance by appropriate blank solns. The e.m.f.-spectrophotometric method used for determining m_{HA} and m_{A^-} in eqn (2) is that originally described by Robinson[11] and subsequently modified[8,9] using the appropriate buffers from the tables of Bates and Gary.[7] The spectrophotometer was a manual Beckmann D.U. instrument with the cells thermostatted to ±0.05°. The thermodynamic pK_a values obtained over the temperature range of operation are given in Table 2.

Table 1. Thermodynamic acidity constants of 1 and 2-naphthol at 25°

	Buffer	Table number*	Ionic strength of buffer	Absorption wavelength(n.m.) of base form	pK_a
1-Naphthol	Borax($Na_2B_4O_7$)-Sodium Chloride	13	0.01	333	9.414
	"	"	0.02	247	9.416
	"	"	0.04	247	9.416
2-Naphthol	Monoethanolamine-Hydrochloric Acid	17	0.02	238	9.572
	"	"	0.04	238	9.580
	"	"	0.08	238	9.572
	Borax($Na_2B_4O_7$)-Sodium Chloride	13	0.04	238	9.570

* These numbers refer to the buffer tables of ref.7

Table 2. Thermodynamic acidity constants (pK_a ± 0.003) of 1 and 2-naphthol

Temp./°C	1-Naphthol	2-Naphthol
5	9.707	9.829
10	9.627	9.758
15	9.552	9.692
20	9.482	9.629
25	9.416	9.573
30	9.358	9.517
35	9.303	9.465
40	9.252	9.418
45	9.205	9.373
50	9.163	9.332
55	9.124	
60	9.089	

Table 3. Thermodynamic functions of ionisation of 1 and 2-naphthol

Compound	ΔG°_{25} [cal/mole]	ΔH°_{25} [cal/mole]	$-\Delta S^\circ_{25}$ [cal/mole.deg]	$-\Delta Cp^\circ_{25}$ [cal/mole.deg]
1-Naphthol	12,804.1±0.4	5034±20	26.06±0.04	45±3
2-Naphthol	13,012.9±0.6	4577±30	28.29±0.05	30±3

DISCUSSION

Our pK_a values for 1- and 2-naphthol are not inconsistent with recently published values.[1-5] Our values at 25° agree to ±0.02 pK_a units with those of Bryson and Matthews and this agreement is satisfactory in consideration of the limited precision of their values.

While van Gemert's value for 2-naphthol at 21° is some 0.08 pK_a units higher than our own value and this seems well above his experimental uncertainty. The agreement between van Gemert's pK_a value for 1-naphthol and our own value is very good. The calculation of thermodynamic parameters from the pK_a values obtained by the spectrophotometric method is complicated by the fact that most acid ionisations show a marked deviation from a linear plot of pK_a vs $1/T$ due to the inadequacy of the assumption of constant ΔH in the integrated form of the van't Hoff equation. Various equations have been applied to these curves and of these the most sucessful have been the Harned-Robinson[12] the Everett and Wynne-Jones[13] and the Clarke-Glew[14] equations.

However it has been shown that the Harned-Robinson equation when fitted to the ionisation constants of phenols[8,9] and benzenethiols[11] gives the same values of ΔG°_{25}, ΔH°_{25} and ΔS°_{25} as the other two equations, within the precision of the spectrophotometric technique. Therefore in this present work the thermodynamic functions of ionisation of 1- and 2-naphthol have been calculated simply by using the Harned-Robinson equation.[12]

The results are presented in Table 3. The most obvious feature of these results is that the ΔH° do not parallel the ΔG° values. It has been shown[16] that this is often the case for many weak acids of not very different acidity strength in aqueous solution. In fact Bell[16] states that caution is necessary in interpreting small differences in pK_a at a single temperature. Expressed another way the relative acidities of 1- and 2-naphthol in water appear to be determined by an entropy (solvation) rather than an enthalpy effect and this is probably related to stronger solvation by water of the 2-naphtholate ion. It was previously observed[8,9] that substituted phenols show good linear correlation between ΔG°_{25} and ΔS°_{25}. The main conclusion which may be drawn from this relationship is that the phenol series is governed by the same substituent interaction mechanism in the ionisation reaction. Because 1- and 2-naphthol lie on the same straight line they very likely share with the phenols this common mechanism where the more delocalised 1-naphtholate ion experiences a smaller degree of solvation and therefore exhibits a less negative ΔS° value.

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