Thermodynamic Acid Dissociation Constants of Aromatic Thiols

By **Paolo De Maria, Adamo Fini,** and **Francis M. Hall,** Istituto di Chimica degli Intermedi, Università di Bologna, Viale Risorgimento 4, 40136 Bologna, Italy

The thermodynamic acid dissociation constants of thiophenol and a series of *meta*- and *para*-substituted thiophenols have been measured in water at 25 °C by the e.m.f.–spectrophotometric method. The results and the significance of the linear free energy relationship for thiophenols are discussed and compared with the limited data available in the literature.

A RENEWAL of interest in structure–reactivity correlations within a single series of thiophenols has highlighted the scarcity of reliable thermodynamic acid dissociation constants for thiols. In recent years kinetic studies[1-3] on nucleophilic reactions involving thiophenols have been carried out and the results discussed in terms of pK_a values and substituent constants (σ values). In particular the interest is in the effect of the replacement of the oxygen atom in phenol with a sulphur atom.[4]

In spite of such interest, however, very few, if any, thermodynamic acidity constants are available for thiols, although many pK_a values in mixed solvent systems are available. In fact, of the aromatic thiols, only thiophenol itself and *para*-nitrothiophenol have reported pK_a values measured in water,[5-7] and then only with limited precision. For these reasons and because of the apparent failure of thiophenol itself to correlate with Taft σ^* parameters,[5] we have determined the thermodynamic acid dissociation constants, in water at 25 °C, for thiophenol, four *meta*-substituted thiophenols, and six *para*-substituted thiophenols. The substituents have been chosen as representative of a broad spectrum of substituent effects on reactivity.

RESULTS

In determining acid dissociation constants the simplest expression is given by (1) and the pK_a values so calculated

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

would be the classical or concentration acidity constants. If ' pH ' in this expression is replaced by the thermodynamic

---

[1] R. F. Hudson and G. Klopman, *J. Chem. Soc.*, 1962, 1062.

[2] P. De Maria and A. Fini, *J. Chem. Soc. (B)*, 1971, 2335.

[3] P. De Maria, A. Fini, and F. M. Hall, *Chimica e Industria*, in the press.

[4] P. De Maria and A. Fini, *J.C.S. Perkin II*, 1973, 1773.

[5] M. M. Kreevoy, E. T. Harper, R. E. Duvall, H. S. Wilgus, III, and L. T. Ditsch, *J. Amer. Chem. Soc.*, 1960, **82**, 4899; M. M. Kreevoy, B. E. Eichinger, F. E. Stary, E. A. Katz, and J. H. Sellstedt, *J. Org. Chem.*, 1964, **29**, 1641.

[6] A. Albert and G. B. Barlin, *J. Chem. Soc.*, 1959, 2384.

[7] W. P. Jencks and K. J. Salvesen, *J. Amer. Chem. Soc.*, 1971, **93**, 4433.

acidity function value $p(a_H\gamma_{Cl})$,[8] then for an acid of charge type -1 [8] the thermodynamic acidity constant may be calculated from equation (2) provided the initial concentration of the acid HA is sufficiently low to allow substitution of concentration terms for activities.

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

The term $[HA]/[A^-]$ is the ratio of acid to salt of the weak acid in the buffer solution. This simplified equation (2) has been successfully used to determine thermodynamic pK_a values for a wide range of substituted phenols [9] and 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 for this present series of thiophenols, thiophenol itself was determined at various ionic strengths. The values obtained agree within experimental error.

m-Nitrothiophenol [15] was prepared by reduction of the commercial disulphide with glucose in alkaline ethanol solution, b.p. 125—126° at 0·5 mmHg.

Dissociation Constant Determinations.—A well known problem encountered with thiophenols is the aerial oxidation of their solutions, especially in alkaline medium; [16] as a result deaeration with nitrogen of all solutions during all stages of preparation was carried out, although in acid medium care must be taken to ensure no loss of the thiophenol by volatilization.

Any oxidation products are extremely insoluble and may be filtered off quite readily before spectrophotometric measurements are made. It is of interest that no spectral interference did occur due to the oxidation products.

The e.m.f.–spectrophotometric method used for determining [HA] and $[A^-]$ in equation (2) is that originally described by Robinson [17] and subsequently modified [9] using the appropriate buffers from the tables of Bates and Gary.[8]

Thermodynamic pK_a values and experimental conditions of measurement. Molality of thiophenols in all cases *ca.* 10^{-4}

Substituent	Thermodynamic pK_a values ($\pm$ 0·005) at 25 °C	Buffer system table no.[a]	Ionic strength (*m*) of buffer	Absorption wavelength (nm) of base form
p-Me (1)	6·820	11	0·04 0·06	266
p-OMe (2)	6·775	11	0·04	264
m-Me (3)	6·660	11	0·04	265
H (4)	6·615	11	0·02 0·04 0·06 0·08	263
	6·5[5] [b]			
	6·43[7] [b]			
m-OMe (5)	6·385	11	0·04	264
p-Cl (6)	6·135	10	0·041	273
p-Br (7)	6·020	10	0·041	273
m-Cl (8)	5·780	10	0·041	269
p-COMe (9)	5·330	10	0·041	345
m-NO_2 (10)	5·241	10	0·041	276
p-NO_2 (11)	4·715	8	0·0418	410
	4·50[7] [b]			

[a] These numbers refer to the buffer table numbers of ref. 8. [b] Published pK_a values.

A simple correction,[10,11] was made for the small change in the buffer ' pH ', due to the presence of the low concentrations (*ca.* 10^{-4}M) of thiophenols used in the spectrophotometric measurements. The Table gives the thermodynamic acidity constant values for the thiophenols studied, as well as the important experimental details.

EXPERIMENTAL

Thiols.—Commercially available substituted thiophenols were carefully distilled or recrystallized just prior to use: thiophenol, b.p. 60—62° at 15 mmHg; *p*-MeO, b.p. 100—102° at 13 mmHg; *p*-Me, m.p. 41—43° (sublimation); *m*-Me, b.p. 83—84° at 14 mmHg; *p*-Cl, m.p. 51—53° (sublimation); *p*-Br, m.p. 75—76° (from ethanol); *p*-NO_2, m.p. 75—77° (from carbon tetrachloride). The following three substituted thiophenols were prepared by the action of *O*-ethyl dithiocarbonate on the appropriate diazotized anilines and subsequent hydrolysis of the esters: *p*-COMe,[12] b.p. 85—87° at 0·2 mmHg; *m*-Cl,[13] b.p. 86—88° at 14 mmHg; *m*-OMe,[14] b.p. 112—114° at 20 mmHg.

The spectrophotometer was a manual Beckmann D.U. instrument with a cell compartment thermostatted to 25 ± 0·1 °C. The absorbance by each solution, namely the buffer solution 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 solutions.

DISCUSSION

Our value for thiophenol in water is not inconsistent with previous values [5,7] especially when such values do not claim to be thermodynamic. Kreevoy [5] in fact states his values are not thought to differ from the true thermodynamic values in water by more than his experimental uncertainty of *ca.* 10%, while Jencks' values [7] were determined at ionic strength 1·0. The variation of some 0·2 pK_a units between our values

---

[8] R. G. Bates and R. Gary, *J. Res. Nat. Bur. Stand.*, 1961, **65A**, 495.

[9] P. D. Bolton, F. M. Hall, and I. H. Reece, *Spectrochim. Acta*, 1966, **22**, 1149, 1825; *J. Chem. Soc.* (*B*), 1966, 717; 1967, 709.

[10] R. A. Robinson and A. K. Kiang, *Trans. Faraday Soc.*, 1955, **51**, 1398.

[11] P. D. Bolton and F. M. Hall, *Austral. J. Chem.*, 1967, **20**, 1797.

[12] H. Egli and G. Schwarzenbach, *Helv. Chim. Acta*, 1934, **17**, 1176; E. Rudin and G. Schwarzenbach, *ibid.*, 1939, **22**, 360.

[13] T. Van Hore, *Chem. Z.*, 1927, 51.

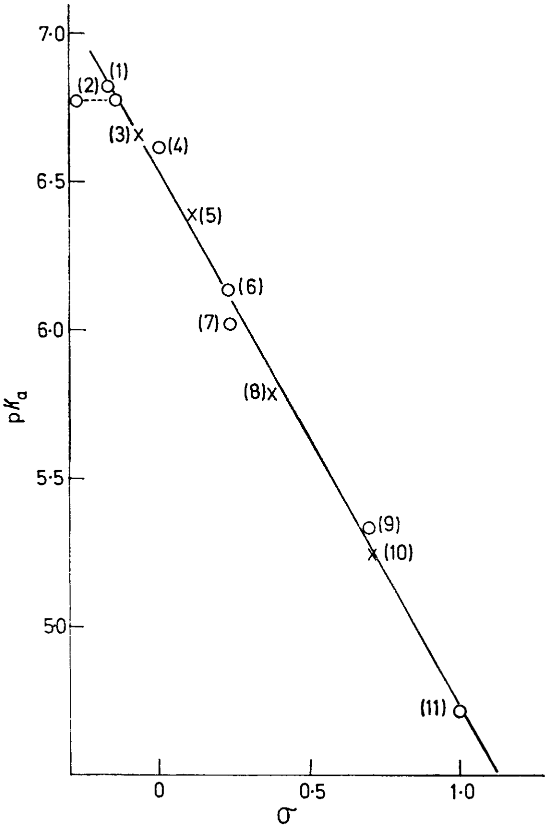
[14] F. Mauthner, *Ber.*, 1906, **39**, 3593.

[15] R. Leuckart and W. Holtzapfel, *J. prakt. Chem.*, 1890, **41**, 197.

[16] F. G. Bordwell and H. M. Andersen, *J. Amer. Chem. Soc.*, 1953, **75**, 6019.

[17] R. A. Robinson and A. I. Biggs, *Trans. Faraday Soc.*, 1953, **51**, 901.

and those of Jencks[7] for both thiophenol and *p*-nitrothiophenol is of an order that could reasonably be expected even though such a large ionic strength is beyond the scope of such expressions as the Debye–Hückel equation.



Hammett plot for ionization of substituted thiophenols. Numbering as in Table

The Figure is a plot of our pK_a values against the substituent constants and shows a high order of linearity. The slope ρ is —1·81 ± 0·1 and the correlation coefficient *r* is 0·997 (least squares). For most substituents the normal Hammett σ values have been used, but different values for σ were necessary for the substituents *p*-NO_2,[16,18] *p*-COMe,[18] and *p*-OMe.

For *p*-OMe two σ values (both used in the Figure) are available, the ordinary Hammett value of —0·27 and the Taft σ^0 value of —0·12, recently successfully adopted by Crampton[19] in correlating the pK_a of some thiophenols bearing substituents not capable of direct mesomeric interaction with the reaction centre. Independently Chuchani[20] has proposed for this same substituent a value of —0·14. While the value fits our linear free energy relationship very well, the significance of such a fit remains difficult to describe.

Although considerable variation[18] in the substituent constant is typical for the *p*-OMe group, which behaves much like the *p*-OH group,[21] the pK_a of *p*-methoxythiophenol appears anomously low when used for kinetic studies. In fact systematic positive deviations from Brønsted-type plots (log *k vs.* pK_a) have been found in nucleophilic reactions involving both substitution[1] and addition.[2]

Recently we have shown[3] that more linear rate–equilibria relationships for thiophenols are generally achieved when pK_a values are replaced by the appropriate carbon basicity[19] values.

We acknowledge financial support by C.N.R. (Roma).

[3/1266 *Received*, 15*th June*, 1973]

---

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

[19] M. R. Crampton, *J. Chem. Soc.* (*B*), 1971, 2112.

[20] G. Chuchani and A. Frohlich, *J. Chem. Soc.* (*B*), 1971, 1417.

[21] F. G. Bordwell and P. J. Boutan, *J. Amer. Chem. Soc.*, 1956, **78**, 87, 854.