

Thermodynamic Functions of Proton Ionization of *para*-Substituted Benzenethiols

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ΔG^0_{25} , ΔH^0_{25} , and ΔS^0_{25} values for ionization of four *para*-substituted benzenethiols have been calculated from thermodynamic pK_a values determined in water over a range of temperatures. These, together with earlier results for *meta*-substituted benzenethiols, show that effects on the free energy of ionization for benzenethiols are primarily related to changes in entropy and that these compounds cannot be considered as forming an isoenthalpic series.

We have recently reported¹ thermodynamic functions of proton ionization for a series of *meta*-substituted benzenethiols. These data demonstrated that the greater acidity, in water, of benzenethiols, when compared with the analogous phenols, resulted from more favourable enthalpies and entropies of ionization. However the relationship between any two of ΔG^0 , ΔH^0 , and ΔS^0 has not been clearly established, and in this paper we have extended our studies by determining thermodynamic data for a series of *para*-substituted benzenethiols in order to clarify these relationships.

¹ P. De Maria, A. Fini, and F. M. Hall, *J.C.S. Perkin II*, 1975, 1540.

² P. De Maria, A. Fini, and F. M. Hall, *J.C.S. Perkin II*, 1973, 1969.

³ R. G. Bates and R. Gary, *J. Res. Nat. Bur. Stand., Sect. A*, **65**, 495.

⁴ P. De Maria, A. Fini, and F. M. Hall, *J.C.S. Perkin II*, 1974, 1443.

EXPERIMENTAL

The benzenethiols studied were commercial samples suitably purified as previously described.² The buffers used were selected from among those described by Bates and Gary,³ such that their acidity functions, $p(a_H\gamma_{Cl})$, were as near as possible to the pK_a values of the chosen benzenethiols.² The e.m.f.-spectrophotometric method used for determining the pK_a values over a range of temperatures has also been previously described.^{1,2,4} The experimental pK_a values so obtained (Table 1) are considered accurate to ± 0.005 units. The thermodynamic parameters evaluated from the experimental pK_a values, using both the Harned-Robinson⁵ and Clarke-Glew⁶ equations are given in Table 2.

⁵ H. S. Harned and R. A. Robinson, *Trans. Faraday Soc.*, 1940, **36**, 973.

⁶ E. C. W. Clarke and D. N. Glew, *Trans. Faraday Soc.*, 1966, **62**, 539.

DISCUSSION

The present and earlier results¹ show that the ΔG_{25}^0 and ΔS_{25}^0 functions of ionization of *meta*- and *para*-substituted benzenethiols are linearly related, with the weaker acids showing greater entropy loss.

TABLE 1

Thermodynamic acidity constants ($pK_a \pm 0.005$) of *para*-substituted benzenethiols

Temp. (°C)	<i>p</i> -Methyl	<i>p</i> -Methoxy	<i>p</i> -Chloro	<i>p</i> -Nitro
5	6.950	6.939	6.287	4.829
10	6.914	6.891	6.246	4.796
15	6.880	6.848	6.207	4.765
20	6.850	6.809	6.172	4.737
25	6.820	6.776	6.139	4.711
30	6.797	6.746	6.110	4.687
35	6.774	6.721	6.083	4.665
40	6.753	6.699	6.059	4.645
45	6.735	6.682	6.038	4.626
50	6.718	6.667	6.018	4.610
55	6.704	6.657		
60	6.692	6.649		

The entropy change is least for the *p*-nitro-compound. This is to be expected because the nitro-group is more capable of delocalization of charge than the other substituents. A plot of ΔG_{25}^0 versus ΔS_{25}^0 (Figure 1) has a slope of -340 K which is in good agreement with the value of -218 K predicted from the Bjerrum electrostatic theory.⁷ This same behaviour is present in the phenol series⁸ but the two series of acids lie on separate lines (Figure 1). In other words at the same acidity the benzenethiols have a greater entropy loss than the phenols and this can be attributed to the greater solvation⁹ by water of the undissociated phenols.

able to the *m*- and *p*-nitrobenzenethiols. The difference in ΔS^0 for these two compounds ($7.1 \text{ J mol}^{-1} \text{ K}^{-1}$) could be due to less resonance contribution in the case of the benzenethiolate ion compared with the phenolate ion. However caution should be used¹¹⁻¹⁴ in interpreting differences in entropies of ionization solely in terms of

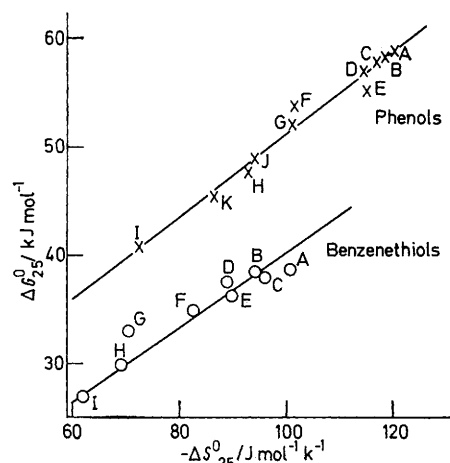


FIGURE 1 Plot of ΔG_{25}^0 versus ΔS_{25}^0 for *m*- and *p*-benzenethiols and -phenols: A, *p*-Me; B, *p*-OMe; C, *m*-Me; D, H; E, *m*-OMe; F, *p*-Cl; G, *m*-Cl; H, *m*-NO₂; I, *p*-NO₂; J, *m*-CN; K, *p*-CN

changes in solvation of the charged members of the acid-base pairs.

A further analysis of the enthalpies and entropies of ionization of the *m*- and *p*-benzenethiols show that neither ΔG^0 nor ΔS^0 show a precise correlation with ΔH^0 . This lack of correlation is evident also for

TABLE 2

Thermodynamic functions of proton ionization of some *para*-substituted benzenethiols

Substituent	$\Delta G_{25}^0 / \text{J mol}^{-1}$	$\Delta H_{25}^0 / \text{J mol}^{-1}$		$\Delta S_{25}^0 / \text{J K}^{-1} \text{ mol}^{-1}$	
		H-R equation *	C-G equation †	H-R equation *	C-G equation †
Me	38 920 \pm 8	9 000	8 800 \pm 200	-100.4	-101.2 \pm 0.4
OMe	38 627 \pm 8	10 700	11 000 \pm 200	-93.3	-94.1 \pm 0.8
Cl	34 991 \pm 4	10 500	10 200 \pm 160	-82.4	-83.7 \pm 0.8
NO ₂	26 878 \pm 8	8 500	8 300 \pm 200	-61.5	-62.3 \pm 0.4

* H-R = Harned-Robinson. † The values for the Clarke-Glew (C-G) equation are the mean obtained from the two and three variable forms of the equation.

The variation in ΔS_{25}^0 values for the ionization of *m*- and *p*-nitrophenols has been attributed to differences in solute-solvent interactions.^{8,10} The relative values of ΔS_{25}^0 for these two phenols can be explained by the assumption that greater delocalization of charge, and therefore less effective solvent ordering, occurs for the *p*-nitrophenoxide ion. This interpretation is also applic-

phenols,⁸ carboxylic acids,¹⁵ and in general for any series of acids where entropy differences are mainly responsible for relative acidities.

Hepler^{10,16} has proposed that the overall effect of a substituent may be divided into internal and external contributions. Based on the assumptions (i) that external contributions to the enthalpy and entropy

⁷ E. J. King, 'Acid-Base Equilibria,' Macmillan, New York, 1965, p. 211.

⁸ J. W. Larson and L. G. Hepler in 'Solute-Solvent Interactions,' eds. J. F. Coetzee and C. D. Ritchie, M. Dekker, New York, 1969, ch. 1, p. 1.

⁹ B. G. Cox, P. De Maria, and A. Fini, *Gazzetta*, in the press.

¹⁰ P. D. Bolton and L. G. Hepler, *Quart. Rev.*, 1971, **25**, 521.

¹¹ G. H. Parsons, C. H. Rochester, and C. E. C. Wood, *J. Chem. Soc. (B)*, 1971, 533.

¹² C. L. Liotta, A. Abidaud, and H. P. Hopkins, jun., *J. Amer. Chem. Soc.*, 1972, **94**, 8624.

¹³ G. H. Parsons and C. H. Rochester, *J.C.S. Perkin II*, 1974, 1313.

¹⁴ C. L. Liotta, H. P. Hopkins, and P. T. Kasudia, *J. Amer. Chem. Soc.*, 1974, **96**, 7153.

¹⁵ J. J. Christensen, R. M. Izatt, and L. D. Hansen, *J. Amer. Chem. Soc.*, 1967, **89**, 213.

¹⁶ L. G. Hepler, *J. Amer. Chem. Soc.*, 1963, **85**, 3089.

changes are related by a constant β and (ii) that the internal contribution to the entropy is negligible, equations (1) and (2) apply. The value of β may vary

$$\Delta G^0 = \Delta H_{\text{int}} + (\beta - T) \Delta S^0 \quad (1)$$

$$\Delta H^0 = \Delta H_{\text{int}} + \beta \Delta S^0 \quad (2)$$

from one reaction to another¹⁷⁻¹⁹ and for phenols values of 240¹⁷ and 190 K¹⁸ have been reported whereas Ives and Marsden²⁰ have postulated that β is actually the temperature of the measurements. In the absence of gas-phase studies which allow the direct calculation of β , we have tentatively assumed for this present series that $\beta = 298$ K. As observed for phenols^{16,17} the substituent induced changes in enthalpy ($\delta\Delta H_{\text{int}}$) for these benzenethiols are very strictly correlated with Hammett's σ values² (Figure 2). An interesting result of this treatment is the comparison of θ with the ratio

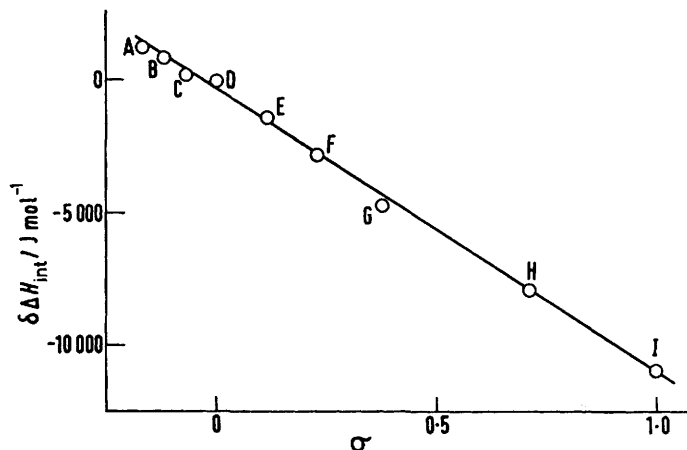


FIGURE 2 Correlation of internal enthalpy components with Hammett's σ values

of the ρ values of benzenethiols² and phenols. θ represents^{17,18} the ratio of the substituent induced internal

enthalpy changes and ρ represents the ratio of the respective free energy changes in aqueous solution.

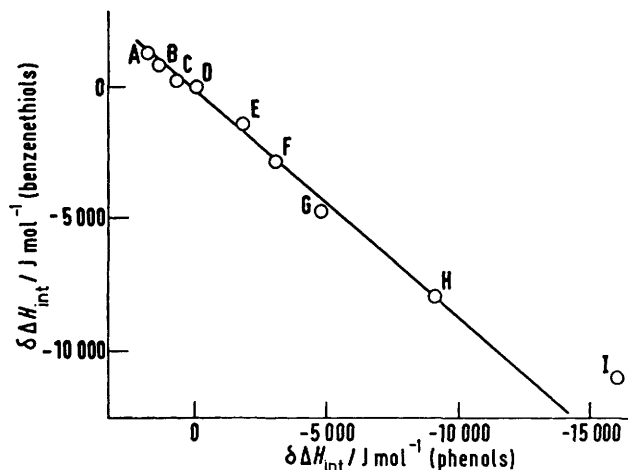


FIGURE 3 Correlation of internal enthalpy components of benzenethiols and phenols

Assuming $\beta = 298$ K then for both series, and neglecting the value for the deviant *p*-nitro substituent (see Figure 3), we obtain equations (3) and (4).

$$\theta = \frac{(\delta\Delta H_{\text{int}})_{\text{benzenethiols}}}{(\delta\Delta H_{\text{int}})_{\text{phenols}}} = 0.85 \quad (3)$$

$$\rho = \rho_{\text{benzenethiols}}/\rho_{\text{phenols}} = 0.82 \quad (4)$$

From such an analysis it may be said that benzenethiols show the same susceptibility to substituent effects, relative to phenols, in both the gas phase and aqueous solution because θ also represents the ratio of the respective free energy changes in the gas phase for these two reaction series.

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¹⁷ P. D. Bolton and F. M. Hall, *J. Chem. Soc. (B)*, 1969, 259.

¹⁸ C. L. Liotta, E. M. Perdue, and H. P. Hopkins, jun., *J. Amer. Chem. Soc.*, 1973, **95**, 2439.

¹⁹ C. L. Liotta, F. M. Perdue, and H. P. Hopkins, jun., *J. Amer. Chem. Soc.*, 1974, **96**, 7308.

²⁰ D. J. G. Ives and P. D. Marsden, *J. Chem. Soc.*, 1965, 649.