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 reported[1] 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.

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–Robinson[5] and Clarke–Glew[6] equations are given in Table 2.

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

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

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DISCUSSION

The present and earlier results[1] show that the ΔG^0_{25} and ΔS^0_{25} 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)	*p*-Methyl	*p*-Methoxy	*p*-Chloro	*p*-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^0_{25} *versus* ΔS^0_{25} (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 series[8] 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 solvation[9] by water of the undissociated phenols.

The variation in ΔS^0_{25} 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^0_{25} 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 applicable to the *m*- and *p*-nitrobenzenethiols. The difference in ΔS^0 for these two compounds (7.1 J mol^{-1} 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 used[11-14] in interpreting differences in entropies of ionization solely in terms of changes in solvation of the charged members of the acid–base pairs.

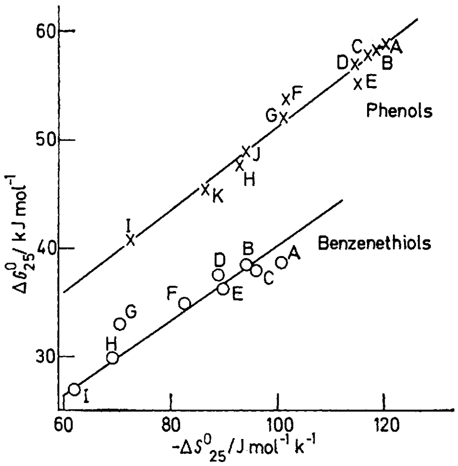

FIGURE 1 Plot of ΔG^0_{25} *versus* ΔS^0_{25} for *m*- and *p*-benzenethiols and -phenols: A, *p*-Me; B, *p*-OMe; C, *m*-Me; D, H; E, *m*-OMe; F, *p*-Cl; G, *m*-Cl; H, *m*-NO_2; I, *p*-NO_2; J, *m*-CN; K, *p*-CN

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

TABLE 2

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

		ΔH^0_{25}/J mol^{-1}		ΔS^0_{25}/J K^{-1} mol^{-1}	
Substituent	ΔG^0_{25}/J mol^{-1}	H–R equation *	C–G equation †	H–R equation *	C–G equation †
Me	38 920 ± 8	9 000	8 800 ± 200	−100.4	−101.2 ± 0.4
OMe	38 627 ± 8	10 700	11 000 ± 200	−93.3	−94.1 ± 0.8
Cl	34 991 ± 4	10 500	10 200 ± 160	−82.4	−83.7 ± 0.8
NO_2	26 878 ± 8	8 500	8 300 ± 200	−61.5	−62.3 ± 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.

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

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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

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

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

from one reaction to another [17-19] and for phenols values of 240 [17] and 190 K [18] have been reported whereas Ives and Marsden [20] 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 values [2] (Figure 2). An interesting result of this treatment is the comparison of θ with the ratio of the ρ values of benzenethiols [2] 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.

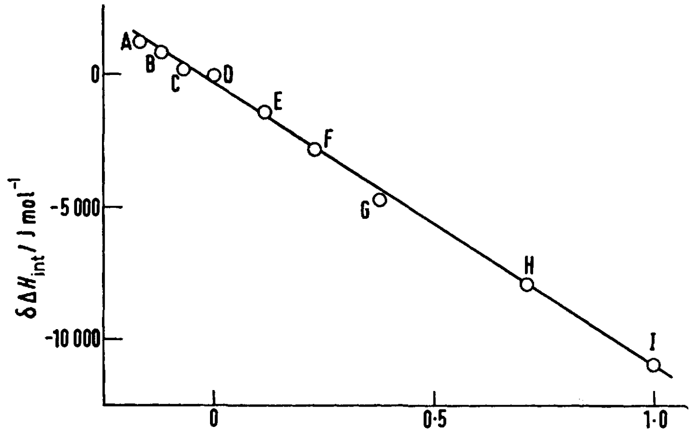

FIGURE 2 Correlation of internal enthalpy components with Hammett's σ values

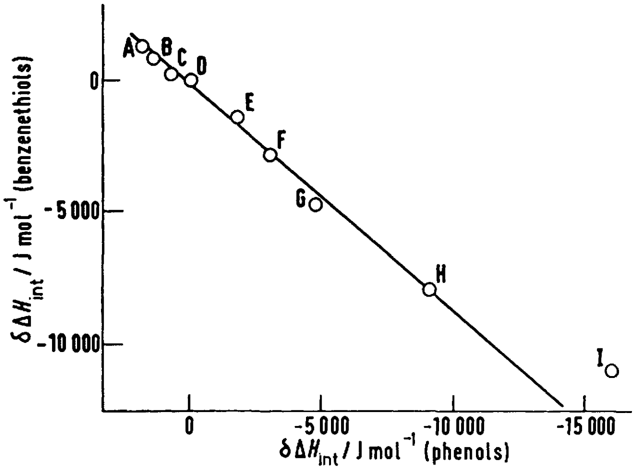

FIGURE 3 Correlation of internal enthalpy components of benzenethiols and phenols

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).

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

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

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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