Thermodynamic Functions of Proton Ionisation of *meta*-Substituted Benzenethiols

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Thermodynamic acidity constants of some *meta*-substituted benzenethiols have been measured spectrophotometrically over a range of temperature in aqueous solution. From these data the thermodynamic functions of ionization, ΔG_{25}, ΔH_{25}, and ΔS_{25}, have been calculated and discussed by means of comparison with the analogous phenols.

In recent years the thermodynamic functions of proton ionization of many aqueous acids have been precisely determined by various methods.[1] The applicability of the e.m.f. spectrophotometric method to obtaining meaningful thermodynamic pK_a data for variously substituted benzenethiols at 25° has been demonstrated.[2,3] Bolton *et al.*[4,5] have described the experimental procedures for determining pK_a values of *meta*-substituted phenols over a range of temperature, and the subsequent evaluation procedures of the thermodynamic functions of ionisation.

An interesting extension of such studies would be to obtain the various thermodynamic functions of ionization for a series of *meta*-substituted benzenethiols and discuss the effect of substitution of SH for OH upon such values.

EXPERIMENTAL

The benzenethiols chosen were either commercial samples, suitably purified, or prepared as previously described.[2] The buffers were selected from those described by Bates and Gary,[6] such that their acidity functions values, $p(a_H\gamma_{Cl})$, were as near as possible to the pK_a values of the benzenethiols under examination.[2] The method used for determining the molalities of protonated and deprotonated benzenethiol, m_{AH} and m_{A^-} respectively, in equation (1) has been previously described.[2,3]

$$pK_a = p(a_H\gamma_{Cl}) - \log(m_{A^-}/m_{AH}) \qquad (1)$$

A manual Beckman DU spectrophotometer with the cells thermostatted to ± 0.05° was adapted for the purpose. The thermodynamic pK_a values obtained over the temperature range of operation are given in Table 1 and the various thermodynamic parameters evaluated from these data, using both the Harned–Robinson[7] and Clarke–Glew equations[8] are given in Table 2. The experimental results obtained for the benzenethiols (Table 2) are not as precise as those obtained for phenols.[4,5] This is probably due to the well known problem of oxidation of benzenethiols in solution[2,3] and also to the overall minor sensitivity of benzenethiol pK_a values to temperature changes.

DISCUSSION

It has been argued[9] that where a substituent affects the change in the free energy of a reaction process through a single interaction mechanism, then an isokinetic-(isoequilibrium) relationship should be observed. Where the substituent acts through a multiplicity of mechanisms, with one mechanism dominating, then a general trend towards a proportionality of any two of ΔG, ΔH, and ΔS will be shown, with some perturbation of the trend caused by the minor mechanisms. For this present series of benzenethiols there is an approximate linear correlation between ΔG and ΔS. However when the pK_a values of these benzenethiols are correlated with the appropriate Hammett σ_m values, the reaction parameter ρ is constant over the whole temperature range (Table 3).

TABLE 1

Thermodynamic acidity constants (pK_a ± 0.005) of benzenethiol and of some *meta*-substituted benzenethiols

Temp. (°C)	Benzenethiol	*m*-Methyl	*m*-Methoxy	*m*-Chloro	*m*-Nitro
5	6.796	6.802	6.518	5.960	5.363
10	6.735	6.757	6.470	5.904	5.324
15	6.687	6.718	6.432	5.858	5.292
20	6.650	6.687	6.407	5.817	5.262
25	6.615	6.660	6.385	5.780	5.235
30	6.586	6.633	6.355	5.746	5.207
35	6.563	6.611	6.330	5.715	5.183
40	6.541	6.592	6.304	5.688	5.158
45	6.518	6.573	6.280		
50	6.499	6.556	6.254		
55	6.481	6.540	6.232		
60	6.469	6.523	6.215		

Such behaviour should arise for an isoenthalpy reaction series which obeys the Hammett equation[5,10] and it has been shown[5] to apply to *meta*-substituted phenols. The observed maximum change in ΔH_{25} for the five benzenethiols under study is 680 cal mol^{-1} (Table 2) and ρ should therefore be expected to show a small temperature dependence if this correlation were carried out over a wider temperature range.

The method of determining an isoequilibrium tem-

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perature, β, by plotting $\delta\Delta H$ against $\delta\Delta S$ (where $\delta\Delta H$ is the substituent-induced change in ΔH, *etc.*) is valueless in this study but for the ionization in solution of these benzenethiols both $\delta\Delta G$ and $\delta\Delta S$ can be obtained. Hence an isoequilibrium temperature can be calculated [5,11] from equation (2) where γ is the slope of a

$$\beta = T + \gamma \qquad (2)$$

linear plot of ΔG against ΔS for the reaction series and T is the absolute temperature.

TABLE 2

Thermodynamic functions of proton ionization of benzenethiol and of some *meta*-substituted benzenethiols

meta- Substituent	ΔG_{25}/ cal mol^{-1}	ΔH_{25}/cal mol^{-1}		ΔS_{25}/cal K^{-1} mol^{-1}	
		H–R equation †	C–G * equation	H–R equation†	C–G * equation
Me	9 082 ± 1	2 270	2 230 ± 48	−22.8	−23.00 ± 0.16
H	9 017 ± 2	2 730	2 648 ± 81	−21.1	−21.35 ± 0.25
OMe	8 694 ± 2	2 330	2 277 ± 54	−21.3	−21.51 ± 0.18
Cl	7 889 ± 1	2 920	2 890 ± 41	−16.7	−16.76 ± 0.14
NO_2	7 138 ± 1	2 250	2 190 ± 46	−16.4	−16.60 ± 0.15

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

TABLE 3

Acidity constants of *meta*-substituted benzenethiols; obedience to the Hammett equation over a range of temperature

Temp. (°C)	ρ	$-\log K_0$	r
5	1.94	6.726	0.997
15	1.92	6.630	0.997
25	1.91	6.560	0.998
35	1.92	6.516	0.996
45	1.91	6.469	0.995

For this present series β = −5 K. It is interesting to note a trend from *meta*-substituted anilinium ions,[12] where β = −1128 K, through *meta*-substituted phenols,[5] β = −69 K, to the *meta*-substituted benzenethiols, *i.e.* a trend towards the more usual 'compensation effect'.[13,14]

From these considerations of our results we conclude that substituent effects on the free energy of ionization of *meta*-substituted benzenethiols are related mainly to changes in entropy and that this present series cannot be described as isoenthalpic. Such conclusions are qualitatively in agreement with those reached by Irving *et al.*[15] in their calorimetric studies on the ionization of thiols in aqueous solutions.

A comparison of the thermodynamic functions of acid ionization of these *meta*-substituted benzenethiols and of their analogous phenols [4,5] shows that the average lowering in free energy is 4500 cal mol^{-1}, the difference arising from the lower enthalpy contribution (2760 cal mol^{-1}) and the higher entropy contribution (5.8 cal K^{-1} mol^{-1}) of the mercapto-group. In other words the greater acidity in water of *meta*-substituted benzenethiols can be considered approximately a 60% enthalpy effect and 40% entropy effect.

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