Thermodynamics of Hydration of 3-Substituted and 3,5-Disubstituted Phenols

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The enthalpies of transfer of 3-chloro-, 3-nitro-, and 3-t-butyl-phenol and their 3,5-disubstituted analogues from the gas phase to aqueous solution are reported together with the corresponding free energies and entropies of transfer for 3-nitro-, 3,5-dinitro-, 3-t-butyl-, and 3,5-di-t-butyl-phenol. The results support previous conclusions that the entropies of ionization of phenols in water are not solely explicable in terms of the electronic effects of ring substituents on the hydration of phenoxide anions. The hydration of the neutral phenols must also be considered and in some cases becomes the predominant factor influencing the effect of substituents on entropies of ionization. Contrary to current theories the solvent ordering effect of phenoxide anions does not always become weaker if substituents are replaced by other substituents which withdraw electronic charge more strongly from the ring position at which the phenoxide oxygen is sited.

STUDIES of the thermodynamics of hydration of phenol, 2-cresol, and several 4-substituted phenols have previously been reported.[1-3] The free energies of hydration were an approximately linear function of the Hammett σ parameters for the substituent groups and the enthalpies of hydration varied in a manner which was correlated empirically with a combined function of the dipole moments and molar volumes of the phenols.[2] The entropy data have shown that the change in the entropy of ionization of phenol caused by 4-substitution arises from partially compensating changes to the entropies of solvation of the neutral phenol and of the phenoxide anion. For the phenols studied so far, apart from 4-bromophenol,[1] the influence of 4-substituents on solute–solvent interactions involving the phenol anions is the dominating factor affecting the entropy of ionization. However explanations (see references cited elsewhere [1]) of differences in entropies of ionization solely in terms of changes in solvation of the charged members of the acid–base pairs are inadmissable. This conclusion has received support from studies of the partial molar volumes and volumes of ionization of phenols both in water [4] and in methanol.[5] The present paper reports measurements of the free energies, enthalpies, and entropies of hydration of 3-t-butyl- and 3-nitro-phenol and their 3,5-disubstituted analogues. The substitution of two identical *meta*-groups in phenol has twice the effect on the free energies and entropies of ionization of phenol than has substitution of one of the groups alone.[6] The influence of successive substitution is additive in this context. It was here required to test whether the correlations and conclusions reached from studies of the hydration of 4-substituted phenols are equally applicable for 3-substituted phenols, and whether the effects of substitution of two groups are additive. Enthalpies of hydration of 3-chloro- and 3,5-dichloro-phenol are also reported.

EXPERIMENTAL

Commercial samples of five phenols were purified by repeated recrystallization from light petroleum (b.p. 40—60°). 3,5-Dinitrophenol was prepared from 3,5-dinitroanisole.[7] The product had m.p. 125—126° (lit.,[7,8] 126°) and has been shown [8] to be the pure phenol and not a dihydrate.[7]

Vapour pressures of the phenols as a function of temperature were determined by a Knudsen effusion method as before.[1] Heats of solution of solid 3-chloro-, 3-nitro-, and 3,5-dichloro-phenol in water were measured with an LKB 8721-1 calorimeter. The thermostat temperature was stable to ±0·002° at 25 ± 0·05° (calibration with N.P.L. thermometer). The solubilities of the other three phenols in water were too low to allow direct calorimetric measurements to be made. The heat of solution of 3,5-di-t-butylphenol was evaluated from measurements (at least ten at each temperature) of the solubility of this phenol in water at four temperatures. The experimental details have already been described.[2] The heats of solution of 3-t-butyl- and 3,5-dinitro-phenol were evaluated from their known enthalpies of ionization in water [6,9] and from calorimetrically measured heats of solution of the solid phenols in aqueous sodium hydroxide solutions. Solubilities of four of the phenols in water were determined as before.[2] The free energies of solution of 3-chloro- and 3,5-dichloro-phenol could not be evaluated from solubility measurements because both phenols gave two immiscible liquid phases in the presence of water.

RESULTS

The vapour pressures of six phenols as a function of temperature are given in Table 1. The free energies, enthalpies, and entropies of sublimation (Table 2) were evaluated from the vapour pressure data as before.[1]

The solubilities of 3,5-di-t-butylphenol in water at four temperatures are given in Table 3. The solubilities at 25° and the free energies, enthalpies, and entropies of solution of 3-nitro-, 3-t-butyl-, 3,5-dinitro-, and 3,5-di-t-butylphenol in water are listed in Table 4. The enthalpies of solution of 3-chloro- and 3,5-dichloro-phenol are included. The latter were calculated using values of 3·76 and 5·50 kcal mol^{-1} for the enthalpies of ionization of 3,5-dinitro- [6]

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

[2] G. H. Parsons, C. H. Rochester, A. Rostron, and P. C. Sykes, *J.C.S. Perkin II*, 1972, 136.

[3] G. H. Parsons and C. H. Rochester, *Chem. and Ind.*, 1972, 604.

[4] C. L. Liotta, A. Abidaud, and H. P. Hopkins, *J. Amer. Chem. Soc.*, 1972, **94**, 8624.

[5] C. H. Rochester and B. Rossall, *Trans. Faraday Soc.*, 1969, **65**, 992, 1004.

[6] P. D. Bolton, F. M. Hall, and J. Kudrynski, *Austral. J. Chem.*, 1968, **21**, 1541.

[7] N. V. Sidgwick and T. W. J. Taylor, *J. Chem. Soc.*, 1922, 1853.

[8] C. H. Rochester, Ph.D. Thesis, London, 1962.

[9] P. D. Bolton, F. M. Hall, and J. Kudrynski, *Austral. J. Chem.*, 1972, **25**, 75.

and 3-t-butyl-phenol [9] respectively and 13·34 kcal mol^{-1} for the enthalpy of self ionization of water.[10] The enthalpies of solution of 3-t-butyl- and 3,5-dinitro-phenol in aqueous sodium hydroxide solutions were measured for concentrations of base of *ca.* 0·1M. The results were not corrected for medium effects incurred by the presence of this concentration of electrolyte. However detailed experiments in which the medium effects were determined for many phenols [11] suggest that the values measured in the present study will be within *ca.* 0·05 kcal mol^{-1} of the true values corrected to infinite dilution of electrolyte. The experiments which enabled the corrections to be made [11] could not be performed for the present two phenols because of the extremely low solubility of the neutral molecules in water.

TABLE 1

Vapour pressures of six phenols as a function of temperature

3-t-Butylphenol						
T/K	299·0	289·8	286·2	273·2	266·4	
10^2P/N m^{-2}	123	51·0	35·9	9·03	3·64	
3,5-Di-t-butylphenol						
T/K	324·5	319·8	313·0	302·8		
10^3P/N m^{-2}	754	507	324	127		
3-Chlorophenol						
T/K	292·5	290·0	284·7	273·2	271·8	251·9
10^3P/N m^{-2}	645	524	294	109	93·9	11·8
3,5-Dichlorophenol						
T/K	295·0	292·0	291·0	288·2	284·2	273·2
10^3P/N m^{-2}	827	612	579	376	275	81·2
3-Nitrophenol						
T/K	333·5	322·5	317·5	312·7	305·5	
10^3P/N m^{-2}	951	359	226	158	73·3	
3,5-Dinitrophenol						
T/K	367·7	348·7	343·0	332·0	329·4	327·2
10^3P/N m^{-2}	106	37·0	25·8	8·72	10·0	10·5

TABLE 2

Thermodynamic parameters * for the sublimation of six phenols at 25°

Phenol	ΔG_1 kcal mol^{-1}	ΔH_1 kcal mol^{-1}	ΔS_1 cal K^{-1} mol^{-1}
3-t-Butylphenol	6·64	17·70	37·1
3,5-Di-t-butylphenol	8·26	15·64	24·7
3-Chlorophenol	5·52	13·77	27·7
3,5-Dichlorophenol	6·79	17·62	36·3
3-Nitrophenol	8·75	18·00	31·0
3,5-Dinitrophenol	10·91	14·60	12·4

* Throughout this paper, 1 cal = 4·184 J.

TABLE 3

The solubility of 3,5-di-t-butylphenol in water at four temperatures

T/K	313·2	308·2	303·2	298·4
10^6 Solubility/molal	150	130	110	100

TABLE 4

Thermodynamic parameters for the solution of six phenols (solid) in water at 25°

Phenol	Solubility molal	ΔG_2 kcal mol^{-1}	ΔH_2 kcal mol^{-1}	ΔS_2 cal K^{-1} mol^{-1}
3-t-Butylphenol	$4{\cdot}593 \times 10^{-3}$	3·19	3·85	2·2
3,5-Di-t-butylphenol	$1{\cdot}000 \times 10^{-4}$	5·46	5·31	−0·5
3-Chlorophenol			2·15	
3,5-Dichlorophenol			4·08	
3-Nitrophenol	$1{\cdot}040 \times 10^{-1}$	1·34	5·86	15·2
3,5-Dinitrophenol	$1{\cdot}425 \times 10^{-2}$	2·52	5·58	10·2

The free energies, enthalpies, and entropies of hydration (transfer from the gas phase to aqueous solution) of the phenols studied here were evaluated [1] (Table 5) from the sublimation and solution data in Tables 2 and 4 respectively. Data for phenol itself [1] are included in Table 5 for comparison with the present results for substituted phenols.

TABLE 5

Thermodynamic parameters for the hydration of seven phenols at 25°

Phenol	ΔG_3 kcal mol^{-1}	ΔH_3 kcal mol^{-1}	ΔS_3 cal K^{-1} mol^{-1}
Phenol	−4·72	−13·61	−29·8
3-t-Butylphenol	−3·45	−13·85	−34·9
3,5-Di-t-butylphenol	−2·80	−10·33	−25·2
3-Chlorophenol		−11·62	
3,5-Dichlorophenol		−13·54	
3-Nitrophenol	−7·41	−12·14	−15·8
3,5-Dinitrophenol	−8·39	−9·02	−2·2

DISCUSSION

The free energies of hydration of 2-cresol, phenol, and five 4-substituted phenols were shown previously to be an approximately linear function of the Hammett σ parameters for the substituents in the phenol ring.[2] The present results for 3-nitrophenol and 3-t-butylphenol and their 3,5-disubstituted analogues are compared in Figure 1 with the results for the other phenols. Values of σ parameters for 3-substituents were taken from the tabulation of Barlin and Perrin.[12] The point in Figure 1 for 3-nitrophenol is in close agreement with the previous correlation but the free energies of hydration of 3-t-butyl-, 3,5-di-t-butyl-, and 3,5-dinitro-phenol

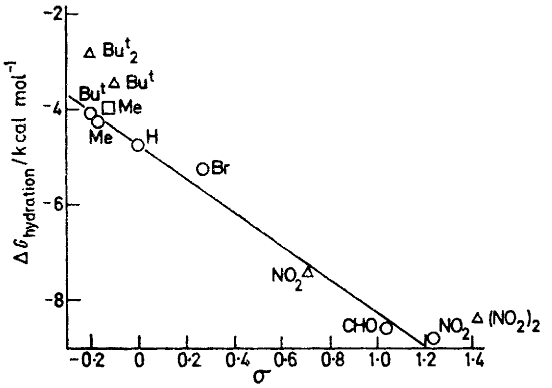

FIGURE 1 Correlation of the free energies of hydration of substituted phenols with the σ-parameters for the substituents: ○, 4-substituted phenols; □, 2-cresol; △, 3- and 3,5-substituted phenols. The line corresponds to equation (2) in ref. 2

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[10] R. N. Goldberg and L. G. Hepler, *J. Phys. Chem.*, 1968, **72**, 4654.

[11] G. H. Parsons and C. H. Rochester, to be published.

[12] G. B. Barlin and D. D. Perrin, *Quart. Rev.*, 1966, **20**, 75.

deviate from the linear plot. However the deviations are insufficient to influence the general observation that the addition of electron-withdrawing substituents decreases (*i.e.* makes more negative) the free energy of hydration of phenol whereas electron-donating substituents increase the free energy of hydration. For both 3,5-di-t-butyl- and 3,5-dinitro-phenol the addition of the first 3-substituent had a larger effect on the free energy of hydration than did the addition of the second substituent. The influence of substituents on the free energies of hydration are therefore not additive since the effect of adding a particular substituent depends upon the groups already present on the phenol ring. Thus the addition of a 5-nitro-group to 3-nitrophenol gives an increment to the free energy of hydration which is only 51% of the corresponding increment for the addition of a 3-nitro-group to phenol itself. Similarly for 3,5-di-t-butylphenol the second t-butyl group gives an increment the magnitude of which is 40% of that for the first group. This contrasts with results for the free energies of ionization of phenols for which, providing steric effects are absent, the effects of substituents are usually additive.[12,13]

It has been noted that there exists an empirical correlation between the enthalpies of hydration of phenol and five 4-substituted phenols and a combined function of the dipole moments and molal volumes of the phenols.[2] However no simple relationship was observed involving the entropies of hydration which appeared to depend on the substituents studied in a rather random and unpredictable manner.[1,2] Combination of our previous results [1,2] with the data in Table 5 now suggests that the trends in the enthalpies and in the entropies of hydration for the overall series of phenols are interrelated. The relationship is illustrated by the graph of entropy of hydration plotted against enthalpy of hydration shown in Figure 2. It is well established that hydrocarbon alcohols give a linear Barclay–Butler plot [14] of entropy against enthalpy of hydration.[15,16] For the series of hydrocarbon alcohols there is a compensation effect between the contributions of the enthalpy and entropy terms to the free energies of hydration. A similar effect has been reported for some fluoro-alcohols although the compensation law plot did not coincide with the corresponding plot for the hydrocarbon alcohols.[17] A single Barclay–Butler plot is apparently only obtained for a series of hydroxylic compounds providing the molecules are of similar chemical character. Thus the results for phenols do not coincide with the results for either hydrocarbon alcohols or fluoro-alcohols although they do give some evidence for compensation effects. Furthermore the experimental points for the phenols themselves apparently fall into two distinct groups (Figure 2). Phenols which contain substituents (CHO or NO_2) which exert a mesomeric effect give an enthalpy–entropy plot which differs from that for the other seven phenols which have been studied. However, even if the division of the phenols into two groups is taken as reasonable, it must be noted that the fitting of the results to straight line plots is much less satisfactory for phenols than for alcohols.[15-17] The wider scatter of points for the former must reflect the existence of specific solvation effects induced by the various different groups which are present as ring substituents in the phenol molecules.

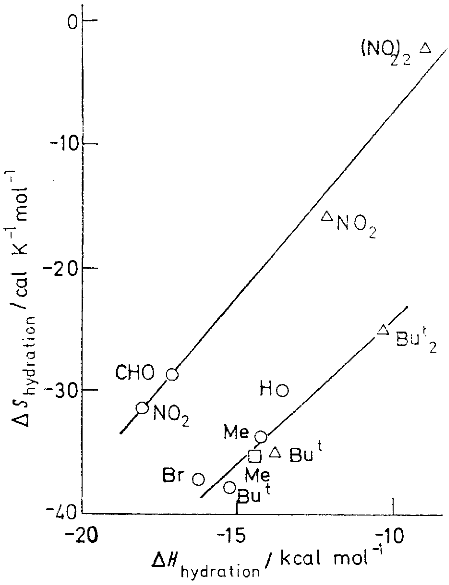

FIGURE 2 Barclay–Butler plot [14] for the hydration of eleven phenols at 298 K: ○, 4-substituted phenols; □, 2-cresol; △, 3- and 3,5-disubstituted phenols

The influence of ring substituents on the thermodynamics of hydration of phenoxide anions has been

$$\begin{tikzcd}
HA_s(g) \arrow[d, "\Delta X_c"'] & + & A_u^-(g) \arrow[r, shift left, "\Delta X_a"] \arrow[d, "\Delta X_d"'] & HA_u(g) \arrow[l, shift left] \arrow[d, "\Delta X_e"'] & + & A_s^-(g) \arrow[d, "\Delta X_f"'] & (1) \\
HA_s(aq) & + & A_u^-(aq) \arrow[r, shift left, "\Delta X_b"] & HA_u(aq) \arrow[l, shift left] & + & A_s^-(aq) & (2)
\end{tikzcd}$$

SCHEME

estimated. The validity of the estimates is dependent upon the applicability of Hepler's [18-23] treatment of the effect of substituents on the thermodynamics of ionization of phenols in water. Consider the Scheme in

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[13] P. J. Pearce and R. J. J. Simkins, *Canad. J. Chem.*, 1968, **46**, 241.

[14] I. M. Barclay and J. A. V. Butler, *Trans. Faraday Soc.*, 1938, **34**, 1445.

[15] J. A. V. Butler, *Trans. Faraday Soc.*, 1937, **33**, 229.

[16] R. Aveyard and A. S. C. Lawrence, *Trans. Faraday Soc.*, 1964, **60**, 2265.

[17] C. H. Rochester and J. R. Symonds, *J.C.S. Faraday I*, 1973, 1577.

[18] W. F. O'Hara and L. G. Hepler, *J. Phys. Chem.*, 1961, **65**, 2107.

[19] L. G. Hepler and W. F. O'Hara, *J. Phys. Chem.*, 1961, **65**, 811.

[20] L. G. Hepler, *J. Amer. Chem. Soc.*, 1963, **85**, 3089.

[21] F. J. Millero, J. C. Ahluwalia, and L. G. Hepler, *J. Chem. Eng. Data*, 1964, **9**, 192.

[22] H. C. Ko, W. F. O'Hara, T. Hu, and L. G. Hepler, *J. Amer. Chem. Soc.*, 1964, **86**, 1003.

[23] P. D. Bolton and L. G. Hepler, *Quart. Rev.*, 1971, **25**, 521.

which HA_s represents a substituted phenol and HA_u is phenol itself. The changes ΔX_a ($X = G, H,$ or S) which accompany reaction (1) give a direct measure of the influence of the substituent in HA_s on the thermodynamics of ionization of phenol in the gas phase. Similarly ΔX_b gives the corresponding effects for the ionization of phenol in water. ΔX_a and ΔX_b are related to the thermodynamic factors, ΔX_c, ΔX_d, ΔX_e, and ΔX_f for the hydration of the four chemical species involved in the equilibria according to equation (3).

$$(\Delta X_b - \Delta X_a) = (\Delta X_f - \Delta X_d) - (\Delta X_c - \Delta X_e) \quad (3)$$

The object of the present calculations was to estimate $(\Delta H_f - \Delta H_d)$ and $(\Delta S_f - \Delta S_d)$ for phenols for which the entropies and enthalpies of ionization are known and for which the enthalpies and entropies of hydration have been reported previously by us.[1-3] The data used in the calculations are given in Table 6. Following our previous nomenclature [1] ΔG_4, ΔH_4, and ΔS_4 refer to the ionization of the phenols in water at 298 K.

TABLE 6

Thermodynamic data at 298 K used in the calculation of the effect of ring substituents on the thermodynamics of hydration of the phenoxide anion. Free energy and enthalpy changes are in kcal mol^{-1} and entropy changes in cal K^{-1} mol^{-1}

Phenol	ΔG_4	ΔH_4	ΔS_4	$(\Delta G_c - \Delta G_e)$	$(\Delta H_c - \Delta S_e)$	$(\Delta S_c - \Delta S_e)$	$(\Delta H_f - \Delta H_d)$	$(\Delta S_f - \Delta S_d)$
Phenol [a,d]	13·63	5·55	−27·1	0	0	0	0	0
2-Methylphenol [a,e]	14·10	5·73	−28·1	0·74	−0·91	−5·6	−1·20	−6·6
4-Methylphenol [a,e]	14·02	5·50	−28·6	0·48	−0·68	−3·8	−1·12	−5·3
4-t-Butylphenol [b,e]	14·05	4·40	−32·4	0·69	−1·64	−7·9	−3·01	−13·2
4-Bromophenol [a,d]	12·74	5·74	−23·5	−0·52	−2·66	−7·2	−1·58	−3·6
4-Formylphenol [a,d]	10·39	4·26	−20·6	−3·86	−3·52	1·1	−1·57	7·6
4-Nitrophenol [a,d]	9·78	4·72	−16·8	−4·04	−4·43	−1·4	−1·41	8·9
3-t-Butylphenol [c]	13·81	5·50	−27·9	1·27	−0·24	−5·1	−0·47	−5·9
3-Nitrophenol [a]	11·41	4·79	−22·2	−2·69	1·47	14·0	2·93	18·9
3,5-Di-t-butylphenol [c]	5·25	14·05	−29·5	1·92	3·28	4·6	2·56	2·2
3,5-Dinitrophenol [a]	3·76	9·19	−18·2	−3·67	4·59	27·6	7·24	36·5

[a] Sources of data for the ionization of these phenols have been tabulated elsewhere (C. H. Rochester in 'The Chemistry of the Hydroxyl Group,' ed. S. Patai, Interscience, London, 1971, p. 327). [b] Data for ionization from ref. 3. [c] Data for ionization from ref. 9. [d] Data for hydration of neutral phenols from ref. 1. [e] Data for hydration of neutral phenols from ref. 2.

The entropy change ΔS_b for a given substituted phenol equals the difference between the entropies of ionization in water of the substituted phenol and phenol itself. Similarly $(\Delta S_c - \Delta S_e)$ is the difference between the entropies of hydration of the substituted and unsubstituted phenols. Following the arguments of Pitzer [24] the Hepler treatment of the effect of substituents on the ionization of phenols is based on the reasonable assumption that ΔS_a approximates to zero providing the acids HA_u and HA_s involved in equilibrium (1) are of closely related structure.[18-23] Hence, taking $\Delta S_a = 0$, $(\Delta S_f - \Delta S_d)$ was evaluated for each phenol *via* equation (3). The values are listed in Table 6.

The enthalpy changes ΔH_b and $(\Delta H_c - \Delta H_e)$ were directly calculable from the known enthalpies of ionization and hydration respectively of the neutral phenols in water. The calculation of ΔH_a is not straightforward. However Hepler [18-23] has established the relationship (4) in which T is the absolute temperature

$$\Delta G_b = \Delta H_a + (\beta - T)\Delta S_b \quad (4)$$

and β is a constant. Experimental evidence has indicated [6,19,20] that β approximately (or exactly? [25]) equals the absolute temperature T and therefore that relationship (5) is applicable. This identity has been

$$\Delta G_b \sim \Delta H_a \quad (5)$$

assumed in the present calculations in which ΔH_a for a particular phenol was taken as the difference between the free energies of ionization of the phenol and of phenol itself in water. Hence [equation (3)] values of $(\Delta H_f - \Delta H_d)$ were deduced (Table 6). It must be emphasized that equations (4) and (5) have been written on the understanding that the thermodynamic changes accompanying the gas-phase reaction (1) are equated with the internal contributions [18-23] to the corresponding changes which occur for reaction (2) in aqueous solution. The external or environmental contributions [18-23] to the latter are entirely attributed to hydration effects, the contributions of which to the thermodynamic changes ΔX_b in water are entirely associated with the relative magnitudes of the hydration terms ΔX_c, ΔX_d, ΔX_e, and ΔX_f.

In Figure 3 the values of $(\Delta S_f - \Delta S_d)$ for eleven phenols have been plotted against the corresponding enthalpy values $(\Delta H_f - \Delta H_d)$. $(\Delta S_f - \Delta S_d)$ and $(\Delta H_f - \Delta H_d)$ are a direct measure of the effect of ring substituents in phenols on the entropy and enthalpy of hydration of the phenoxide anion. Figure 3 is therefore equivalent to a Barclay–Butler plot for the hydration of phenoxide anions with the experimental point for the unsubstituted phenoxide ion placed at the origin of the graph. The similarity between the arrangements of the experimental points in Figures 2 and 3 emphasizes that in general the influence of ring substituents on the enthalpies and entropies of hydration of neutral phenols is to a large extent mirrored by a corresponding influence on the enthalpies and entropies of hydration of the phenoxide anions. Thus only one case was observed (the entropies of hydration of 4-nitrophenol and its

[24] K. S. Pitzer, *J. Amer. Chem. Soc.*, 1937, **59**, 2365.

[25] D. J. G. Ives and P. D. Marsden, *J. Chem. Soc.*, 1965, 649.

anion) in which substitution had opposite effects on the enthalpies or entropies of hydration of phenol and the phenoxide anion. The relative effects of substitution on the entropies and enthalpies of hydration of phenol and phenoxide anions can be evaluated from the data in Table 6. Comparison of $(\Delta S_c - \Delta S_e)$ and $(\Delta S_f - \Delta S_d)$ shows that for seven phenols substitution causes a bigger change in the entropy of hydration of the anion than in the entropy of hydration of the neutral phenol. The change for the anion is smaller for two phenols and opposite in sign to that for the neutral phenol in the particular case of 4-nitro-substitution. The enthalpy changes $(\Delta H_f - \Delta H_d)$ for the phenoxide anions are greater for six phenols but smaller for four phenols than the corresponding changes $(\Delta H_c - \Delta H_e)$ for the neutral molecules. The overall conclusion must be that the influence of substitution on the entropies and enthalpies of hydration of neutral phenols is by no means negligible compared with the influence of the same substituents on the entropies and enthalpies of hydration of phenoxide anions. Thus, in accord with our previous conclusions,[1-3,26] differences between entropies of ionization of substituted phenols in hydroxylic solvents are not wholly explicable in terms of solvation changes involving the phenoxide anions alone. Solvation changes involving the neutral phenol molecules must also be taken into account and apparently become the predominant factor in some cases.

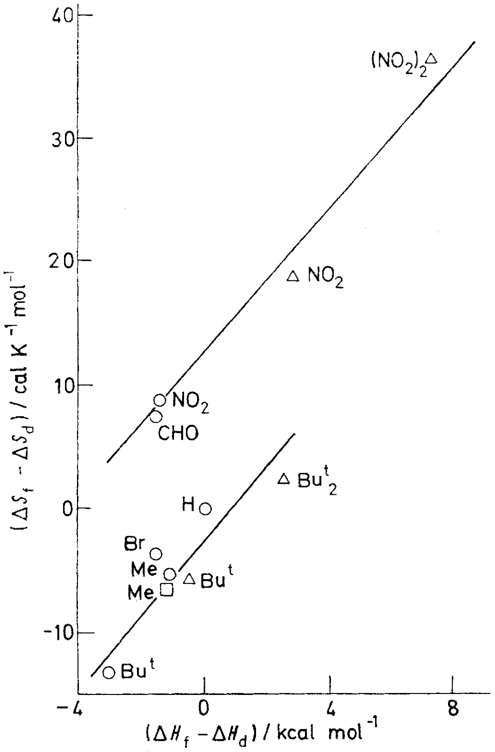

FIGURE 3 Relationship between the estimated effects of ring substitution on the enthalpies and entropies of hydration of some phenoxide anions at 298 K: ○, 4-substituted phenoxide anions; □, 2-methylphenoxide anion; △, 3- and 3,5-substituted phenoxide anions

The use of the identity (5) and the assumption that $\Delta S_a = 0$ providing the acids HA_s and HA_u involved in equilibrium (1) are of closely similar structure implies the equality of ΔG_a and ΔG_b with ΔH_a. This particular form of the Hepler treatment leads [equation (3)] to equation (6). It follows that the influence of a substituent on the free energy of hydration of neutral phenol equals the influence of the same substituent on the free energy of

$$(\Delta G_c - \Delta G_e) = (\Delta G_f - \Delta G_d) \qquad (6)$$

hydration of the phenoxide anion. It is unlikely that this identity will be obeyed because either ΔS_a may not exactly equal zero or β [equation (4)] may deviate from 298 K. The range of values of β which are thought to be reasonably consistent with the observed thermodynamic data for the ionization of phenols in water is 270 K $< \beta <$ 320 K.[20] If $\beta > T$[6] then the effect of substituents on the free energies of hydration will be larger for the neutral phenols than for their anions. If $\beta < T$ then the effects will be bigger for the phenoxide anions. However for all realistic values of β the calculated figures for $(\Delta X_c - \Delta X_e)$ and $(\Delta X_f - \Delta X_d)$, where $X = G, H,$ or S (Table 6), are only effected to a small extent by taking $\beta \neq 298$ K. The general conclusions reached as a result of the present treatment are therefore unaffected by the precise value (here taken as 298 K) of β used in the calculations.

It has already been noted that the changes in the free energy of hydration of neutral phenol caused by the successive addition of two t-butyl or two nitro-groups are not additive. The changes in the enthalpies of hydration for the neutral phenols and their anions are also not additive nor are the entropy effects for successive t-butyl substitution either in phenol or its anion. However the entropy effects for the addition of a 3-nitro-group to phenol or a 5-nitro-group to 3-nitrophenol are apparently almost exactly additive both for the neutral phenols and for the anions. Thus the addition of the nitro-groups to neutral phenol produces successive increments of 14·0 and 13·6 cal K^{-1} mol^{-1} to the entropy of hydration. For the phenol anion the successive increments are 18·9 and 17·6 cal K^{-1} mol^{-1}. The sign of these increments for the hydration of phenoxide anions is consistent with the proposal that electron-withdrawing substituents in the phenol ring delocalize the charge distribution in the anion and therefore decrease the extent of the solute–solvent interaction.[23] However the relative values of $(\Delta S_f - \Delta S_d)$ for 3- and 4-nitrophenol are anomalous in this context. Bolton and Hepler[23] have emphasized that the relative values of the entropies of ionization of these two phenols are explicable on the assumption that greater delocalization of charge and therefore less effective solvent ordering occurs for the 4- than for the 3-nitrophenoxide ion. The present results do not support this conclusion. Thus the entropy of hydration of the 4-nitrophenoxide ion is less (the absolute value will be more negative)

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[26] C. H. Rochester and B. Rossall, *Trans. Faraday Soc.*, 1969, **65**, 992.

than the entropy of hydration of the 3-nitrophenoxide ion. The solvent-ordering effect is therefore apparently greater for the former ion than for the latter. The relative values of the enthalpies of hydration of the two anions support the proposal that 4-nitrophenoxide ions are more strongly solvated than 3-nitrophenoxide ions.

A complete analysis of the relative values of all the entropies (and enthalpies) of hydration of phenoxide anions is not attempted here. However in general the results show that the influence of substituents on solute–solvent interactions involving phenoxide ions is not simply explicable in terms of the delocalization of charge within the ions. Specific effects of the substituent groups on solvation phenomena must also play an important role in the ion–water interaction. It appears that specific effects for the phenoxide anions are at least in part mirrored by parallel specific effects for the neutral phenols. The free energies of ionization therefore reveal a clearer correlation with the electron-withdrawing or -donating capacity of substituent groups.

[4/488 *Received*, 13*th March*, 1974]