

acid, 75 g of potassium acetate, and 75 g of acetic anhydride. The mixture was heated to 95° at which point 19 g of  $\text{KMnO}_4$  were added. The resulting manganic acetate solution was then used for the preparation of various lactones.

**Relative Reactivity of Various Olefins. Competitive Procedure.** In a typical experiment, 20 ml of an acetic acid solution, 0.2 *M* in each of the two olefins under study and 1 *M* in potassium acetate, was mixed with 20 ml of a 0.1 *M* solution of  $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$  in acetic acid, also 1 *M* in KOAc. The reaction mixture was placed in a tube, flushed with nitrogen, and sealed. The reactions were run in a constant-temperature bath maintained at  $130 \pm 1^\circ$  for a period of 1–2 hr, by which time the brown manganic color had disappeared.

When the reaction was over, the tube was cooled, and the reaction mixture was diluted with 200 ml of ether. The ether solution was extracted twice with ice-water and three more times with cold saturated sodium bicarbonate solution. The ether extract was then dried over sodium sulfate, and after filtration the ether was removed on a rotary evaporator. The resulting reaction residue was then analyzed by vapor phase chromatography.

The relative amounts of the two lactones formed were determined from the areas of the corresponding vpc peaks, corrected for differences in response for the two compounds. All reactions were run in duplicate and analyzed twice each by vpc.

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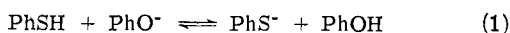
## Thermodynamics of Acid–Base Equilibria. V.<sup>1–4</sup> Ionization of Thiophenol. An Ion Size Effect

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**Abstract:** The thermodynamic parameters  $\Delta\bar{G}^\circ$ ,  $\Delta\bar{H}^\circ$ ,  $\Delta\bar{S}^\circ$ , and  $\Delta\bar{V}^\circ$  have been determined for the ionization of thiophenol in aqueous solution at 25°. These values have been combined with the literature values for the ionization of phenol in aqueous solution at 25°, and the thermodynamic parameters for the proton transfer reaction,  $\text{PhSH} + \text{PhO}^- \rightleftharpoons \text{PhS}^- + \text{PhOH}$ , (1), have been calculated. The gas-phase thermodynamic parameters  $\Delta G^\circ_1(\text{g})$ ,  $\Delta H^\circ_1(\text{g})$ , and  $\Delta S^\circ_1(\text{g})$  have been estimated for eq 1 and compared with the corresponding solution parameters. The results are analyzed in terms of current solution theories. The volume change for eq 1 can be adequately accounted for in terms of van der Waals volumes and the calculated electrostriction of the solvent by the anions. The entropy change for eq 1 could not be completely accounted for by any current theory.

Enthalpies, entropies, and volumes of ionization<sup>5a</sup> provide useful information concerning solute–solvent interactions. Numerous investigators have extensively studied the thermodynamics of ionization of phenol and substituted phenols, as summarized by Larson and Hepler.<sup>5a</sup> The data indicate that the variation of the  $\text{p}K_a$ 's of substituted phenols is almost completely due to changes in the entropy of ionization. In contrast, very few reliable data are available on the sulfur analog of phenol, thiophenol. The  $\text{p}K_a$  of thiophenol has been investigated by several researchers<sup>6,7</sup> and is reported to be approximately 6.5. These results show that thiophenol is considerably more acidic than phenol ( $\text{p}K_a = 9.97$ ). The relative acidities are clearly demonstrated in the proton transfer reaction shown in eq 1 for which the aque-



ous Gibbs free energy of proton transfer [ $\Delta G^\circ_1(\text{aq})$ ] is calculated to be  $-4.75$  kcal/mol.

In this study, the thermodynamic parameters  $\Delta\bar{G}^\circ$ ,  $\Delta\bar{H}^\circ$ ,  $\Delta\bar{S}^\circ$ , and  $\Delta\bar{V}^\circ$  have been determined for the ionization of thiophenol in aqueous solution. The values have been combined with the literature values for the ionization of phenol in aqueous solution at 25° to yield the thermodynamic parameters for eq 1. In addition, the gas-phase thermodynamic parameters  $\Delta G^\circ_1(\text{g})$ ,  $\Delta H^\circ_1(\text{g})$ , and  $\Delta S^\circ_1(\text{g})$  have been estimated by a combination of semiempirical (CNDO/2) results and statistical thermodynamic methods. The thermodynamic functions for the proton transfer reaction are analyzed in terms of current theories in order to approach a better understanding of solute–solvent interactions<sup>5</sup> involved in organic acid–base equilibria.

## Experimental Section

The  $\text{p}K_a$  of thiophenol was determined spectrophotometrically at the absorbance maximum of the thiophenoxide anion ( $37,950 \text{ cm}^{-1}$ ). The extinction coefficients of thiophenol ( $\epsilon_{\text{PhSH}} 560$ ) and

**Table I.** Ionization Data for  $1.005 \times 10^{-4} M$  Thiophenol at  $25^\circ$ 

PhS <sup>-</sup> -PhSH ratio	Ionic strength of buffer	Apparent $pK_a$
3.8515	0.02	6.485
3.7423	0.03	6.479
3.6722	0.04	6.471
3.5706	0.05	6.470
3.4895	0.06	6.467
3.2621	0.10	6.458

<sup>a</sup>  $pK_a$  (at  $I = 0$ ) =  $6.488 \pm 0.003$ .

**Table II.** Enthalpy of Neutralization Data for Thiophenol at  $25^\circ$ 

PhSH, mmol	$-\Delta H_n$ , kcal/mol	PhSH, mmol	$-\Delta H_n$ , kcal/mol
1.002	9.25	1.748	9.33
1.185	9.32	2.040	9.38
1.638	9.33		

<sup>a</sup>  $\Delta H_n(\text{av}) = -9.32 \pm 0.05$ .

the thiophenoxide anion ( $\epsilon_{\text{PhS}^-}$ , 13,130) were determined in  $10^{-4} N$  HCl and  $10^{-3} N$  NaOH, respectively. Absorbance measurements in a standard  $\text{KH}_2\text{PO}_4$ - $\text{Na}_2\text{HPO}_4$  buffer system, for which the acidity function  $p(a_{\text{H}^+\text{Cl}})$  has been determined over a wide ionic strength range, were used to calculate the apparent  $pK_a$  values by the method of Bates and Gary.<sup>8</sup> A correction for the effect of the ionization of thiophenol on the acidity function of the buffer was applied to obtain the true apparent  $pK_a$  values.<sup>9</sup> All absorbance measurements were performed on a Beckman ACTA V spectrophotometer which was equipped with a thermally regulated cell holder ( $25.0 \pm 0.1^\circ$ ).

The enthalpy of neutralization of thiophenol was determined calorimetrically using a solution calorimeter which has been described.<sup>2,3</sup> The Hewlett-Packard Model 3450-A digital voltmeter was used for all voltage measurements. Calorimetric determinations were carried out in a reaction flask containing 1005 ml of water, 1 to 3 mmol of freshly distilled thiophenol, and 0.2815 mmol of perchloric acid which was added to prevent ionization of the thiophenol. During an experiment, a 5-ml sample of 4.83  $N$  sodium hydroxide was introduced into the system. The total enthalpy determined for this reaction is the sum of the enthalpy of dilution of sodium hydroxide from 4.83 to 0.0239  $N$ , the enthalpy of formation of 0.2815 mmol of water from  $\text{H}^+$  and  $\text{OH}^-$ , and the enthalpy of neutralization of thiophenol. From literature data for the enthalpy of dilution of sodium hydroxide<sup>10</sup> and the enthalpy of ionization of water,<sup>5b</sup> the first two terms were calculated to be  $-0.23$  and  $3.76$  cal, respectively. The enthalpy due to neutralization of thiophenol is obtained by subtracting these two terms from the total enthalpy of reaction.

The apparent molal volumes of thiophenol and sodium thiophenoxide in aqueous solution were determined with a high-precision densitometer similar to the apparatus described by Millero.<sup>11</sup> The system was calibrated against the best available data for aqueous sodium chloride solutions.<sup>12</sup>

All solutions used in these studies were prepared from boiled, nitrogen-saturated water. Unless these precautions were taken, rapid oxidation of the thiophenoxide anion occurred, as evidenced by the formation of a white precipitate of phenyl disulfide.

## Results

The apparent  $pK_a$  values determined for thiophenol at several ionic strengths are shown in Table I. Following the procedure of Bates and Gary,<sup>8</sup> these values were extrapolated to infinite dilution to obtain the thermodynamic  $pK_a$  value ( $pK_a = 6.488 \pm 0.003$ ). Previously reported values are 6.50<sup>6</sup> and 6.43.<sup>7</sup>

The results of five determinations of the enthalpy of neutralization ( $\Delta \bar{H}_n$ ) of thiophenol are given in Table II. In all the calorimetric determinations, the ionic strength was less than 0.03. At this ionic strength, the difference between the enthalpies of dilution of sodium hydroxide and sodium thiophenoxide is estimated to be negligible, so that the standard

**Table III.** Apparent Molal Volume for Thiophenol and Sodium Thiophenol at  $25^\circ$ 

Molality	Density, g/ml	NaOH-NaSPH ratio	$\phi_v$ , ml/mol
Thiophenol			
$5.39 \times 10^{-3}$	0.997161		94.06
$4.39 \times 10^{-3}$	0.997145		94.12
Sodium Thiophenoxide			
$2.20 \times 10^{-2}$	0.999361	1.16	80.40
$1.05 \times 10^{-2}$	0.998843	2.61	80.35
$4.59 \times 10^{-3}$	0.997408	0.44	80.19
$3.63 \times 10^{-3}$	0.997405	0.89	80.29
$1.67 \times 10^{-3}$	0.997403	3.21	80.19

state infinite dilution value for  $\Delta \bar{H}_n$  is taken to be the average of the values given in Table II. When  $\Delta \bar{H}_n^\circ = -9.32$  kcal/mol is combined with the enthalpy of ionization of water,<sup>5</sup> the standard enthalpy of ionization of thiophenol is calculated to be  $\Delta \bar{H}_i^\circ = 4.02 \pm 0.08$  kcal/mol. Combining  $\Delta \bar{H}_i^\circ$  with the thermodynamic  $pK_a$  yields the standard entropy of ionization of thiophenol ( $\Delta \bar{S}_i^\circ = -16.2$  cal/(deg mol)).

The density data and the derived apparent molal volumes ( $\phi_v$ ) of thiophenol and sodium thiophenoxide are given in Table III. King<sup>13</sup> has shown that for an acid whose degree of ionization ( $\alpha$ ) is small, the concentration dependence of  $\phi_v$  can be given by

$$\phi_v = \bar{V}^\circ + B(1 - \alpha)C \quad (2)$$

where  $\bar{V}^\circ$  is the standard partial molal volume,  $B$  is a constant, and  $C$  is the stoichiometric concentration of the acid. Because of the low solubility of thiophenol and the limiting sensitivity of the densitometer, the concentration range which could be studied was small. Since the degree of ionization is less than 1%, and the values given in Table III agree within experimental uncertainty, the standard partial molal volume of thiophenol is the average of the values given in Table III ( $\bar{V}^\circ(\text{PhSH}) = 94.10 \pm 0.05$  ml/mol).

Millero<sup>14</sup> has shown that the volume of a dilute mixed electrolyte solution can be adequately represented by a linear combination of the  $\phi_v$  values of the individual electrolytes at the ionic strength of the solution; *i.e.*, Young's rule<sup>15</sup> is obeyed to within 2% for the majority of 1:1 electrolytes up to high concentrations. Utilizing this principle, the total volume of a solution is

$$V = (1000/d^0) + m_2\phi_2 + m_3\phi_3 \quad (3)$$

which can be arranged to give

$$\phi_2 = \frac{1000}{m_2} \left[ \frac{d^0 - d}{dd^0} \right] + \left[ \frac{M_2 + aM_3}{d} \right] - a\phi_3 \quad (4)$$

where  $\phi_2$  and  $\phi_3$  are the apparent molal volumes of the two electrolytes,  $d^0$  and  $d$  are the densities of pure water and the solution, respectively,  $M_2$  and  $M_3$  are the molecular weights of the two electrolytes,  $m_2$  and  $m_3$  are the molalities of the two electrolytes, and  $a = m_3/m_2$ . Using eq 4, the apparent molal volume ( $\phi_v$ ) of sodium hydroxide<sup>16</sup> at the ionic strength of the solution was combined with the experimentally determined densities to yield  $\phi_v$  values for sodium thiophenoxide. The  $\phi_v$  values for sodium thiophenoxide were then plotted vs.  $I^{1/2}$  and extrapolated to zero ionic strength to obtain the standard partial molal volume of sodium thiophenoxide [ $\bar{V}^\circ(\text{Na}^+, \text{PhS}^-) = 80.1 \pm 0.05$  ml/mol].

The partial molal volume of completely ionized thiophenol,  $\bar{V}^\circ(\text{H}^+, \text{PhS}^-)$ , can be calculated from  $\bar{V}^\circ(\text{Na}^+, \text{PhS}^-)$  by adding [ $\bar{V}^\circ(\text{H}^+) - \bar{V}^\circ(\text{Na}^+)$ ] = 1.20 ml/mol.<sup>13</sup> When

**Table IV.** Comparison of the Thermodynamics of Ionization of Thiophenol and Phenol at 25°<sup>a</sup>

	$\Delta\bar{G}^\circ$	$\Delta\bar{H}^\circ$	$\Delta\bar{S}^\circ$	$\Delta\bar{V}^\circ$
PhSH	8.85	4.02	-16.2	-12.76
PhOH	13.60 <sup>b</sup>	5.48 <sup>b</sup>	-27.2 <sup>b</sup>	-18.01 <sup>c</sup>
Eq 1 (aq)	-4.75	-1.46	11.0	5.25
Eq 1 (g)	-30.41	-31.09	-2.05	

<sup>a</sup>  $\Delta\bar{G}^\circ$  and  $\Delta\bar{H}^\circ$  values in kcal/mol;  $\Delta\bar{S}^\circ$  values in cal/(deg mol);  $\Delta\bar{V}^\circ$  values in ml/mol. <sup>b</sup> Reference 5, <sup>c</sup> Reference 33.

$\bar{V}^\circ$  ( $\text{H}^+$ ,  $\text{PhS}^-$ ) is combined with  $\bar{V}^\circ$  (PhSH),  $\Delta\bar{V}^\circ_i$  for the ionization of thiophenol is calculated to be -12.8 ml/mol.

## Discussion

For proton transfer reactions such as eq 1, it is convenient for interpretation purposes to divide the changes observed in the thermodynamic functions into two parts,<sup>5</sup> *i.e.*, an "internal" (int) and an "environmental" (en) contribution. The "internal" contributions are those effects which are intrinsic to the molecule, whereas the environmental effects are a consequence of the interaction of the solutes with the solvent. The two contributions for several of the observed changes in the thermodynamic state function for eq 1 have been estimated by means of current theories and combined for a comparison with the experimental values.

## Volume Analysis

The "internal" contribution to  $\Delta\bar{V}^\circ_i$  can be considered to consist of two items: (1) the van der Waals volumes of the solutes and (2) the void spaces created by the introduction of the solute into the solvent. Bondi<sup>17</sup> has assembled a table of representative van der Waals radii and volume increments which can be combined with the available bond lengths and ionic radii to yield estimates for the van der Waals volumes of each solute in eq 1. For the bond lengths of C-O, O-H, C-S, and S-H, the values found<sup>18</sup> in methanol and methanethiol were used. The ionic radii<sup>19</sup> of  $\text{O}^-$  and  $\text{S}^-$  were combined with the neutral molecule C-O and C-S bond lengths to yield the volume of the anions. The derived van der Waals volumes for PhSH, PhOH,  $\text{PhS}^-$ , and  $\text{PhO}^-$  are 59.30, 53.51, 67.50, and 55.41 ml/mol, respectively. A convenient method for the estimation of  $\Delta V_{\text{int}}$  assumes that the void volume contribution is zero. Applying this method with the above values yields  $\Delta V_{\text{int}} = 6.1$  ml. Alternatively,  $\Delta V_{\text{int}}$  can be estimated from a suitable theory of solutions which takes into account the perturbation of the solvent structure by the solute.

The scaled particle theory of fluids developed by Reiss, *et al.*,<sup>20</sup> provides an expression for the Gibbs free energy of cavity formation for the introduction of a hard sphere solute into a hard sphere fluid. Pierotti<sup>21</sup> has demonstrated that this result is an excellent approximation for real systems, that can be combined with the molecular properties of the solvent and solute to successfully predict the solubility, enthalpy of solution, and partial molal volume of gases dissolved in numerous solvents, including water. When this method is applied to the species in eq 1, the molecular cavity volume,  $V_c$ , calculated for PhOH, PhSH,  $\text{PhS}^-$ , and  $\text{PhO}^-$ , is 92.66, 101.24, 112.60, and 95.41 ml/mol, respectively. These values yield an estimate of  $\Delta V_{\text{int}} = 8.62$  ml.

The estimation of the environmental contribution,  $\Delta V_{\text{en}}$ , requires a detailed knowledge of the intermolecular forces acting between the solvent and solute molecules. While the general nature of these forces are known for neutral species,<sup>22</sup> a quantitative theory for the calculation of the volume effects associated with these interactions is not available.

When the cavity volume and the compressibility contribution of the solvent are subtracted<sup>21</sup> from the experimental  $\bar{V}^\circ$  values, an estimate of -7.15 and -6.43 ml/mol is obtained for the environment component of  $\bar{V}^\circ$  for PhSH and PhOH, respectively. This result suggests that the contribution of the neutral species to  $\Delta V_{\text{en}}$  for eq 1 is small. However, it is well known that the volume effects associated with the electrostriction of ions<sup>23</sup> are quite large and might be expected to be the major contribution to  $\Delta V_{\text{en}}$ .

The electrostriction volume change,  $\Delta V_{\text{elec}}$ , of the solvent due to the presence of an ion can be estimated from the Born equation<sup>23</sup> or the rigorous thermodynamic analysis of Frank<sup>24</sup> for a fluid in an electrostatic field. Previous attempts to apply these two theories to estimate the magnitude of electrostriction have been reviewed by Conway,<sup>25</sup> Friedman and Krishnan,<sup>23</sup> and Millero.<sup>26</sup>

Bernal and Fowler<sup>27</sup> originally pointed out that the collapse of the water structure near the ion was probably the major contribution to electrostriction in water solutions. The method of Desnoyers, Verrall, and Conway<sup>28</sup> based on the equations of Frank<sup>24</sup> provides a means whereby the volume changes accompanying this solvent collapse can be estimated. King<sup>13</sup> has shown that this method can be adequately applied to carboxylate anions to yield reasonable results for organic systems. Consequently, this is the method preferred by the authors of this paper.

In order to calculate the electrostriction term by the Desnoyers, Verrall, and Conway<sup>28</sup> method, it is necessary to evaluate the average electrostatic field in the first solvent layer immediately around the charge on the ion. The average electric field,  $E$ , in any water layer around the ion is  $E = Ze/er^2$ , where  $Ze$  is the charge on the ion,  $r$  is the distance from the center of the ion to the center of the water layer, and  $\epsilon$  is the dielectric constant in this layer. If  $r$  can be established,  $\epsilon$  can be found by simultaneous solution of the field relationship and the empirical equation,<sup>29</sup> relating  $\epsilon$  to  $E$ .

For monoanions, it is sufficient<sup>28</sup> to consider only those water molecules in the first layer around the ion. However, before  $\Delta V_{\text{elec}}$  for any ion can be calculated by this theory, a molecular model must be constructed which predicts the average number of water molecules which are in intimate contact with the charge. King<sup>13</sup> has recently utilized this theory to estimate the electrostriction around a formate ion by arbitrarily assuming that two water molecules are associated with each oxygen. Since it is impossible at this time to establish unambiguously the average number of water molecules in the immediate vicinity of the charge for the two anions in eq 1,  $\Delta V_{\text{elec}}$  is calculated using two solvation models.

The distance from the center of the charge in each anion to the center of the water layer nearest the charge was taken to be the sum of the radius of a water molecule (1.38 Å) and the van der Waals radii of  $\text{O}^-$  or  $\text{S}^-$ , respectively. At this distance, the average  $E$  was calculated as indicated above, and the molar volume of water in this field was obtained from the equation of Desnoyers, *et al.*<sup>28</sup> If an average coordination of two is assumed for both the phenoxide and thiophenoxide anions, the value of  $\Delta V_{\text{elec}}$  for eq 1 is +0.84 ml/mol. Alternatively, the maximum number of water molecules that could be influenced by the electric field can be estimated from the volume accessible to water molecules around the atoms containing the charge in the anions. It is estimated from molecular models that the phenyl group effectively prohibits one-half the primary solvation layers of  $\text{S}^-$  and  $\text{O}^-$  from containing water molecules. Since the volume of the primary solvation layers,  $V_s$ , can easily be calculated from the van der Waals radii, the maxi-

**Table V.** Calculated Gas-Phase Entropies of Thiophenoxide and Phenoxide Anions

Entropy contribution <sup>a</sup>	Thiophenoxide anion	Phenoxide anion
Translational	39.979	39.505
Rotational	26.389	25.493
Vibrational	8.611	6.965
Total	74.979	71.963

<sup>a</sup> All values in cal/(deg mol).

imum number of water molecules in the primary layer around each of the anions can be estimated as  $V_s/2\bar{V}$ , where  $\bar{V}$  is the molar volume of water in the electric field. The value of  $\Delta V_{elec}$  for eq 1 determined from this model is  $-0.28$  ml/mol. Although the  $\Delta V_{elec}$  values calculated from the two solvation models differ in sign, the magnitude of the  $\Delta V_{elec}$  obtained is approximately zero. These results indicate that the contribution of  $\Delta V_{elec}$  to the overall volume change is small for the anions in eq 1.

When  $\Delta V_{int}$  derived from van der Waals volumes ( $\Delta V_w = 6.10$  ml/mol) is combined with the  $\Delta V_{elec}$  values calculated by the method of Desnoyers, *et al.*,<sup>28</sup>  $\Delta V^\circ_1$  is predicted to fall between 5.82 and 6.94 ml. A similar analysis using  $\Delta V_{int}$  derived from the scaled particle theory ( $\Delta V_c = 8.62$  ml) predicts  $\Delta V^\circ_1$  to be between 8.34 and 9.46 ml. Using either model, the agreement between predicted and observed  $\Delta V^\circ_1$  is good. In addition, the results indicate that the  $\Delta V^\circ_1$  is primarily due to  $\Delta V_{int}$  and only slightly influenced by variations in solute-solvent interactions.

### Entropy Analysis

The internal contribution to  $\Delta\bar{S}^\circ_1$ , defined in this discussion as the standard gas-phase entropy of proton transfer ( $\Delta S_{int}$ ), can be obtained from the gas phase entropies determined experimentally or estimated from statistical mechanical calculations. The bond lengths used in the volume analysis were also used to calculate the moments of inertia of the anions. An assignment of the fundamental vibrational frequencies for the anions is available from a comparison of the infrared and laser Raman spectra<sup>30</sup> of the sodium salts with the assignments which have been determined for thiophenol<sup>31</sup> and phenol.<sup>32</sup> All of the low-frequency fundamentals were found either in the infrared or Raman spectra of the sodium salts. Consequently, the vibrational contribution to the entropies of the anions is estimated to within  $\pm 0.2$  cal/(deg mol). Table V summarizes the translational, rotational ( $\sigma = 2$ ), and vibrational contributions for each anion. The calculated entropies of the anions have been combined with the experimentally derived entropies of thiophenol<sup>31</sup> ( $\bar{S}^\circ_g(\text{PhSH}) = 80.51$  cal/(deg mol)) and phenol<sup>32</sup> ( $\bar{S}^\circ_g(\text{PhOH}) = 75.44$  cal/(deg mol)) to yield  $\Delta\bar{S}^\circ_g$  for eq 1 ( $\Delta S_{int} = -2.05$  cal/(deg mol)).

From a thermodynamic cycle, the external contribution to the entropy of proton transfer is given by

$$\Delta S_{ext} = -\Delta\bar{S}^\circ_{hyd}(\text{PhSH}) - \Delta\bar{S}^\circ_{hyd}(\text{PhO}^-) + \Delta\bar{S}^\circ_{hyd}(\text{PhS}^-) + \Delta\bar{S}^\circ_{hyd}(\text{PhOH})$$

The entropies of hydration of the neutral molecules can be calculated from the experimentally determined entropies of solution and vaporization. At 25°, the equilibria, solid phenol  $\rightleftharpoons$  aqueous phenol, does not exist, but a metastable equilibria of this type is reported by Jones<sup>33</sup> to occur at 0°. The solubility at 0° can be combined with the enthalpy of solution<sup>34</sup> at 25° to yield the necessary solubility for the metastable equilibria at 25°. When the vapor pressure data of Biddlescombe and Martin<sup>35</sup> is combined with the solution parameters, a value of  $\Delta\bar{S}^\circ_{hyd}(\text{PhOH}) = -29.4 \pm 0.2$

cal/(deg mol) is obtained. The entropy of hydration of thiophenol has been determined from the vapor pressure data of Scott<sup>31</sup> and the temperature dependence of the limited solubility of thiophenol<sup>36</sup> as  $\Delta\bar{S}^\circ_{hyd}(\text{PhSH}) = -30.8 \pm 1.0$  cal/(deg mol). Consequently it is evident that the neutral species contribute only a small fraction to the total  $\Delta S_{en}$  for eq 1 since the  $\Delta\bar{S}^\circ_{hyd}$  for phenol and thiophenol are identical within experimental error. The difference between the hydration entropies of the anions is a direct measure of the contribution of the anions to  $\Delta S_{en}$ .

Qualitatively, the positive value found for  $\Delta S_{en}$  for the anions (11.65 cal/(deg mol)) is in agreement with the prediction of simple electrostatic theory<sup>37</sup> if the charge of the anions is assumed to be primarily localized on the sulfur and oxygen atoms as indicated by the CNDO/2 results. The positive difference is predicted on the basis of the larger radius of  $\text{S}^-$  compared with  $\text{O}^-$ . If, however, simple electrostatic theory is quantitatively correct, then the ratio of  $\Delta S_{elec}$  to  $\Delta V_{elec}$  should be equal to the theoretical constant 2.39 cal/(cm<sup>3</sup> deg), where  $\Delta S_{elec}$  and  $\Delta V_{elec}$  are the entropy and volume changes for eq 1 resulting from the electrostatic interactions of the anions with the solvent. The ratio derived from simple electrostatic theory is dependent only on the macroscopic properties of the solvent which are well known for water.<sup>37</sup> A maximum estimate of  $\Delta V_{elec}$  can be derived by combining  $\Delta V_{int}$  with  $\Delta V_1$  if  $\Delta V_{en}$  is assumed to be totally due to electrostriction effects of the anions. Values of  $-0.85$  and  $-3.36$  ml/mol can be obtained for  $\Delta V_{elec}$  when the van der Waals and scaled particle  $\Delta V_{int}$  values are subtracted from  $\Delta V^\circ_1$ . Using these values, the  $\Delta S_{elec}$  predicted for eq 1 by simple electrostatic theory is between  $-2.0$  and  $-8.0$  cal/(deg mol). These values have the wrong sign since the experimentally based  $\Delta S_{ext}$  for the anions is positive, *i.e.*,  $+11.65$  cal/(deg mol). Therefore the entropy-volume relationship of electrostatic theory is seen to give completely incorrect results. King<sup>15</sup> has also shown that simple electrostatic theory cannot account for the entropy change observed for similar proton transfer reactions in carboxylic acids. It now appears that the entropy-volume relationship derived from simple electrostatic theory is of little value in the correlation of these two thermodynamic parameters in organic acid-base equilibria.

Since it is reasonable to assume that the negative charge of the anions is somewhat localized on the oxygen or sulfur (CNDO/2 results), a modified version of the Born equation, which includes the effects of dielectric saturation of the solvent, can be employed to provide a direct estimate<sup>38</sup> for  $\Delta S_{elec}$ . In order to apply this theory, it is necessary to assume that the phenyl group will cause approximately the same change in the electrostatic interactions for both  $\text{O}^-$  and  $\text{S}^-$ . With this assumption as a first approximation,  $\Delta S_{elec}$  for eq 1 is the difference between the entropies of  $\text{O}^-$  and  $\text{S}^-$  calculated from the modified Born equation. The predicted  $\Delta S_{elec}$  found from this approach is 2.05 cal/(deg mol), which has the correct sign but accounts for only one-sixth of the experimental value. A resonance interaction of the phenyl group to delocalize the charge can be shown to be greater for the phenoxide anion by simple orbital size arguments or from the CNDO/2 results. Consequently, any arguments based on resonance delocalization of the charge in the anion would decrease the value of  $\Delta S_{elec}$  predicted by the Born theory.

From the preceding discussion, it is clear that while the volume change observed for eq 1 can be satisfactorily accounted for in terms of a van der Waals contribution and a small contribution due to electrostriction, there is no current theory to quantitatively account for the large positive  $\Delta S^\circ_1$  value observed for eq 1. King<sup>13</sup> has concluded in a

similar analysis of the entropy and volume changes observed for several carboxylic acids that the entropy-volume correlation predicted by the Born equation may not exist for the ionization process of organic acids. The results obtained in our analysis of the thermodynamic parameters for eq 1 further substantiates this conclusion.

### $\Delta G^\circ$ Analysis

The internal contribution of  $\Delta G^\circ_1$  is best determined from ion cyclotron resonance studies. Unfortunately, the experimental data for the ionization of thiophenol are not available. However, Taft, *et al.*,<sup>3,9</sup> have shown that the gas-phase results on the relative proton affinities of several pyridines agree reasonably well with the values calculated by the CNDO/2 method. Therefore, the CNDO/2 results of Henneike<sup>40</sup> for each species in eq 1 have been combined to yield an estimate for  $\Delta E^\circ_1(\text{g}, 0^\circ\text{K}) = -31.1$  kcal/mol. This result is only 20% larger than the value of  $-37.7$  kcal/mol predicted from the bond dissociation energies of SH and OH<sup>41</sup> and the electron affinities of oxygen and sulfur.<sup>42</sup> When the CNDO/2 results are combined with the statistical mechanical calculations based on the molecular parameters and spectroscopic data,  $\Delta G^\circ_1(\text{g}, 298^\circ\text{K}) = -30.41$  kcal/mol. A comparison of this value with the aqueous  $\Delta G^\circ_1 = -4.75$  kcal/mol emphasizes the importance of environmental effects on the relative acidities of these organic acids, *i.e.*,  $\Delta G_{\text{en}} = +25.66$  kcal/mol. An analysis of  $\Delta G_{\text{en}}$  based on the vapor pressure and solubility data used in the entropy analysis yields  $\Delta G_{\text{hyd}}(\text{PhOH}) = -4.71$  kcal/mol and  $\Delta G_{\text{hyd}}(\text{PhSH}) = -0.53$  kcal/mol. From these values, the difference between the  $\Delta G_{\text{hyd}}$  values for PhS<sup>-</sup> and PhO<sup>-</sup> is calculated to be  $+29.85$  kcal/mol. As in the entropy analysis, it is seen that the anions are the major cause of the large environmental term.

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