# Heats of Ionization of Some Phenols and Benzoic Acids in Dimethyl Sulfoxide. Heats of Solvation of Oxyanions in Dimethyl Sulfoxide and Water

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**Abstract:** Heats of ionization for nine phenols and four benzoic acids in $Me_2SO$ are reported. Substituent effects on heats of solution from the gas phase to water and $Me_2SO$ are estimated from heats of transfer from carbon tetrachloride to these solvents. The data are combined to calculate heats of solvation to phenoxide anions in both solvents and benzoate ions in $Me_2SO$. Ionization properties are compared in the gas phase, water, and $Me_2SO$.

## Introduction

The ability of phenols and benzoic acids to ionize as Bronsted acids in the convenient aqueous pH range has cast them in a key role for development of quantitative theories of substituent effects.[1-10] Beyond using their dissociation constants as a reference point for empirical free-energy relationships, several workers have explored other thermodynamic properties of ionization. Thus Hepler and his associates[3,11-13] found that in some cases the differences in free energy of ionization in water for phenols are determined entirely by entropy differences which they attributed to solvation of the phenoxide ions. A study by Bolton, Fleming, and Hall[10] demonstrates a beautiful correlation between $\Delta G_i°$ and $\Delta S_i°$ for benzoic acids in water, the variation in $\Delta H_i°$ terms being very small in this solvent. However, Matsui, Ko, and Hepler[14] have reported discrepancies in some of the values in that report and hence on the validity of the correlation. Liotta[15] has confirmed Hepler's analysis of entropy terms but has found that the volumes of ionization in water primarily reflect substituent effects on the partial molar volume of the neutral phenol.

The effect of solvent change on ionization has been discussed in general by Bell[9] and for phenols in particular by Bolton,[16-18] Stewart,[19] and Rochester.[20-23] Against this background, there is now good appreciation that solvent effects on ionization can only be analyzed definitively in terms of substituent effects on the solvation properties of the neutral acids and of their anions. Several attempts[15,21] have been made to accomplish such an analysis through indirect estimation of the gas-phase ionization properties. However, recent gas-phase measurements by McIver[25] using ion cyclotron resonance and Kebarle[26] using high-pressure mass spectrometry now permit complete experimental resolution of solvation properties of all species concerned.

Elsewhere we have described methods for determining the heats of ionization for a wide range of acids and heats of solvation of their anions in $Me_2SO$.[27-30] Those reports focused on the behavior of acids which are too weak to ionize appreciably in dilute aqueous base. This article presents our results for some phenols and benzoic acids in $Me_2SO$ and compares enthalpies of solvation of the neutral acids and their anions in $Me_2SO$ and water.

## Experimental Section

Solvents were purified, stored, and used as described previously.[30,31] The water content of $Me_2SO$, determined by Karl Fischer titration, was maintained below 75 ppm and that of $CCl_4$ below 25 ppm through storage over molecular sieves. Potassium dimsylate was also prepared and used as before.[30,32] Phenols and benzoic acids were commercially available and were purified until physical and spectral properties verified their purity.

Solution calorimetry employed the apparatus and techniques described previously in connection with this project.[30-32]

## Results

In Table I are presented the partial molar enthalpies of solution for the acids treated here in $Me_2SO$, $K^+DMSYL^-$, $CCl_4$, and $H_2O$. From these values are derived the heats of deprotonation: $\Delta H_D = \Delta\overline{H}_S{}^{K^+DMSYL^-} - \Delta\overline{H}_S{}^{Me_2SO}$ and heats of transfer from $CCl_4$ to $Me_2SO$ or from $Me_2SO$ to $H_2O$.

All heats of solution reported here are based on at least six separate measurements in the same calorimeter. No trends were observed as the concentration of solute varied over a range from about $10^{-3}$ to $10^{-2}$ M. In this connection, the question arises as to whether the phenols were ionized to a significant extent in pure water. Using available p$K_a$'s in the range 7 to 10,[7] it is obvious that dissociation is less than 0.1% for all except *p*-nitrophenol, which is still only 0.63% ionized.

The cycle which was used to calculate heats of solvation of the anions employed phenol as a reference compound as follows:

$$\begin{tikzcd}
 & \mathrm{AH} \arrow[dd, "(\mathrm{AH})", "\Delta\overline{H}_S"'] & + & C_6H_5O^- \arrow[r] \arrow[dd, "(C_6H_5O^-)", "\Delta\overline{H}_S"'] & A^- \arrow[dd, "(A^-)", "\Delta\overline{H}_S"'] & + & C_6H_5OH\ (\text{gas}) \arrow[dd, "(C_6H_5OH)", "\Delta\overline{H}_S"'] \\
\text{or} & & & & & & \\
 & \mathrm{AH} & + & C_6H_5O^- \arrow[r] & A^- & + & C_6H_5OH\ (\text{solution})
\end{tikzcd}$$

Heats of deprotonation in the gas phase are derived from McIver's[25] and Kebarle's[26] work. The heats of deprotonation come from data in Table I.

The necessary data to complete the cycle in order to calculate the heats of solvation of the anions $A^-$ relative to phenoxide ion are the heats of solution of the neutral acids AH (i.e., phenols and benzoic acids) relative to phenol from the gas phase to high dilution in water or $Me_2SO$ [i.e., $\delta\Delta\overline{H}_S{}^{g\rightarrow Me_2SO} = \Delta\overline{H}_S(\mathrm{AH}) - \Delta\overline{H}_S(C_6H_5OH)$]. In principle, this merely involves subtracting the heat of vaporization or sublimation of AH from the heat of solution of its pure liquid or crystalline state into $Me_2SO$ or water. In practice, this term may be badly in error because of serious discrepancies in heats of vaporization or, more often, heats of sublimation.

Pilcher and Cox[33] and Driesbach[34] have provided valuable tabulations of thermodynamic data for vaporization. Thompson's definitive[35] review describes and evaluates the methods for determination of vapor pressures. Although it is frequently feasible to measure heats of vaporization and sublimation directly with high precision,[36] there are often serious problems that arise with individual compounds. These difficulties can produce enormous discrepancies when data obtained at different times by different methods in different laboratories are compared. Chickos[37] discusses this problem

**Table I.** Measured Heats of Solution at 25 °C for Pure Phenols and Benzoic Acids

| Compound | $\Delta\overline{H}_S^{Me_2SO}$ | $\Delta\overline{H}_S^{K^+DMSYL^-}$ | $\Delta\overline{H}_S^{CCl_4}$ | $\Delta\overline{H}_S^{H_2O}$ |
|---|---|---|---|---|
| 1. Phenol | −0.72 ± 0.01 | −25.0 ± 0.4 | 6.27 ± 0.07 | 2.7 ± 0.1 |
| 2. *o*-Cresol | 0.0 ± 0.10 | −24.92 ± 0.3 | 8.21 | 3.19 ± 0.05 |
| 3. *m*-Cresol | −2.78 ± 0.05 | −26.97 ± 0.2 | 3.72 ± 0.1 | 0.73 ± 0.02 |
| 4. *p*-Cresol | −1.00 ± 0.10 | −23.60 ± 0.4 | 5.85 ± 0.3 | 2.94 ± 0.04 |
| 5. *o*-Chlorophenol | −4.86 ± 0.09 | −33.67 ± 0.3 | 1.55 ± 0.08 | −0.08 ± 0.02 |
| 6. *m*-Chlorophenol | −4.22 ± 0.20 | −31.33 ± 0.5 | 3.28 ± 0.1 | 0.67 ± 0.02 |
| 7. *p*-Chlorophenol | −0.97 ± 0.06 | −26.74 ± 0.7 | 6.74 ± 0.17 | 3.82 ± 0.1 |
| 8. *p*-*tert*-Butylphenol | 1.08 ± 0.07 | −22.11 ± 0.3 | 6.72 ± 0.2 | |
| 9. *p*-Nitrophenol | −0.86 ± 0.10 | −33.8 ± 0.5 | 8.46 | 5.66 ± 0.1 |
| 10. Benzoic acid | 1.26 ± 0.01 | −32.8 ± 0.4 | 3.71 ± 0.11 | |
| 11. *p*-Chlorobenzoic acid | 2.74 ± 0.15 | −32.0 ± 0.3 | 3.56 ± 0.06 | |
| 12. *p*-Fluorobenzoic acid | 1.70 ± 0.22 | −32.9 ± 0.3 | 4.13 ± 0.09 | |
| 13. *p*-Methoxybenzoic acid | 3.06 ± 0.15 | −30.5 ± 0.4 | 2.04 ± 0.09 | |

and points to the case of naphthalene for which reported heats of sublimation range from 8.0 to 19.6 kcal/mol. We have also found enough disagreement between tabulated[33,34] values for phenols and benzoic acids to have grave reservations about any individual value which has not been checked repeatedly by different investigators.

However, for the purpose of calculating solvation enthalpies of anions for the present and related studies,[27-29] the heats of vaporization/sublimation are simply a means to an end, viz., the calculation of *relative* heats of solution for a series of structurally related compounds from the gas phase to $Me_2SO$ ($\delta\Delta\overline{H}_S^{g\rightarrow Me_2SO}$) or to water ($\delta\Delta\overline{H}_S^{g\rightarrow H_2O}$).

On the basis of a number of recent studies, we have concluded that heats of transfer from an aprotic nonpolar solvent to $Me_2SO$ or water are a more reliable guide to $\delta\Delta\overline{H}_S^{g\rightarrow Me_2SO}$ or $\delta\Delta H_S^{g\rightarrow H_2O}$ than are many of the values derived from vaporization/sublimation data. For this purpose we have used $CCl_4$ as our reference "inert" solvent since all compounds considered here are relatively soluble in it. Support for this approach may be found in the work of Krishnan and Friedman,[38] Drago,[39-41] Fuchs,[42] and Arnett and Wolf.[43] In essence, the approach assumes that for a series of similar compounds, the differences between the heats of solution from the gas phase to a highly polar solvent (such as $Me_2SO$) and from the gas phase to an inert solvent ($CCl_4$) will have a small nonspecific additive component related to molecular volume and the difference in cohesive energy densities of the two solvents.[44] There may also be a much larger component due to specific factors, such as hydrogen bonding, which would be reflected both in $\delta\Delta H_t^{CCl_4\rightarrow Me_2SO}$ and $\delta\Delta H_S^{g\rightarrow Me_2SO}$ (t, transfer). Since hydrogen bonding from phenol to $CCl_4$ is thermochemically negligible,[40,54] this contribution would be the same whether phenol were transferred to $Me_2SO$ from the gas phase or from $CCl_4$. The present treatment is a reasonable extension of regular solution theory[24,45,46] and is probably accurate to ±0.5 kcal/mol in most cases. Since there are few solutes of relevance to this study whose heats of sublimation are known with that reliability, it is not easy to check satisfactorily. However, in Figure 1 we have plotted $\delta\Delta H_t^{CCl_4\rightarrow Me_2SO}$ vs. $\delta\Delta\overline{H}_S^{g\rightarrow Me_2SO}$ for a few compounds where all data seem reliable. The correlation is fair (0.985), and we have used the slope −1.5 to convert $\delta\Delta\overline{H}_t^{CCl_4\rightarrow Me_2SO}$ to estimate $\delta\Delta H_S^{g\rightarrow Me_2SO}$ values to be presented below. A referee has expressed well-founded skepticism of this procedure and notes that points 4–7 for aliphatic alcohols generate an entirely different slope.

## Discussion

The data to be considered here may be compared in a variety of ways. We will approach them first by contrasting thermodynamics of ionization in water, where they are reliably known, with the same properties in the gas phase and in $Me_2SO$. We will then use the enthalpies of ionization in all three media and the estimated enthalpies of transfer from the gas phase to compare interaction of the neutral acids with the two solvents. Finally, we will compare the derived solvation enthalpies for their anions.

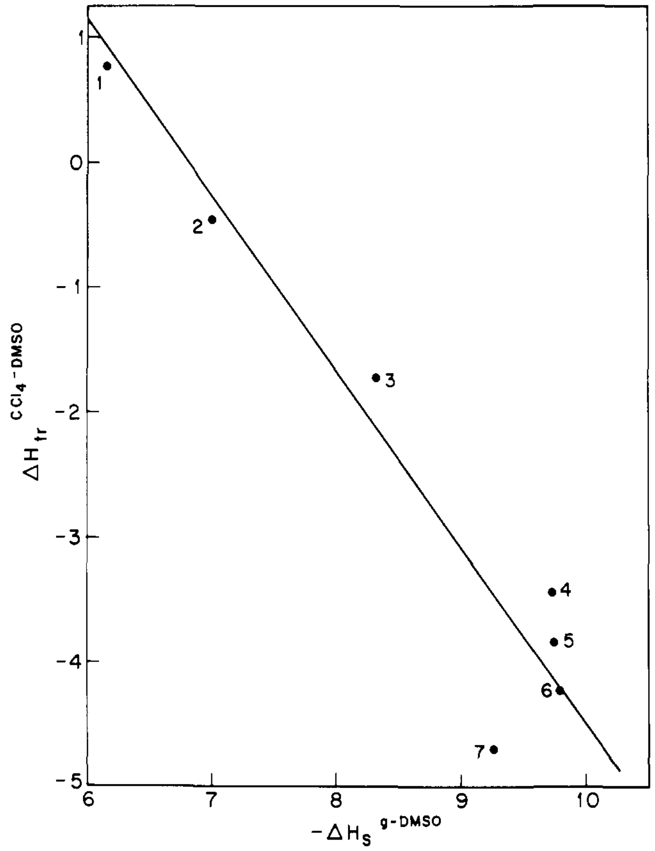

Figure 1. Heats of transfer from carbon tetrachloride to $Me_2SO$ vs. heats of solution from gas phase to $Me_2SO$ for cyclopentadiene (1), acetone (2), acetonitrile (3), *n*-butyl alcohol (4), *n*-propyl alcohol (5), ethanol (6), methanol (7).

**Ionization Thermodynamics.** In Table II we present a variety of free energy and enthalpy data for ionization of phenols and benzoic acids in water, $Me_2SO$, and the gas phase. All values are taken relative to phenol by subtracting its measured value (in brackets beneath first line) from that measured for AH. Thus, the property in each case is for the proton transfer process:

$$AH + C_6H_5O^- \rightarrow A^- + C_6H_5OH$$

It has proved to be a good assumption that entropy terms for

**Table II.** Ionization Properties for Phenols and Carboxylic Acids in Water, $Me_2SO$, and the Gas Phase

| | $\delta\Delta G_i°$(gas) | | $\delta\Delta G_i°$ | | $\delta\Delta H_i°$ | |
|---|---|---|---|---|---|---|
| AH | McIver | Kebarle | $H_2O^a$ | $Me_2SO$ | $H_2O^a$ | $Me_2SO$ |
| 1. Phenol | 0 | 0 | 0 | 0 | 0 | 0 |
| (absolute) | | (339)$^d$ | (13.60) | (24.7) | (5.48) | (−24.3 ± 0.4) |
| 2. *o*-Cresol | −0.3 | −0.7 | 0.50 | −0.6 | 0.22 | −0.6 |
| 3. *m*-Cresol | 0.5 | 0.4 | 0.18 | 0.1 | 0.02 | 0.1 |
| 4. *p*-Cresol | 1.2 | 1.3 | 0.42 | 1.7 | 0.02 | 1.7 |
| 5. *o*-Chlorophenol | −4.6 | −6.3 | −1.93 | −4.51 | −1.08 | −4.51 |
| 6. *m*-Chlorophenol | −6.1 | −7.9 | −1.16 | −2.8 | −0.28 | −2.8 |
| 7. *p*-Chlorophenol | −2.9 | −6.6 | −0.74 | −1.5 | 0.20 | −1.5 |
| 8. *p*-*tert*-Butylphenol | −0.6 | | 0.35 | 1.1 | | 1.1 |
| 9. *p*-Nitrophenol | | −25.8 | −3.84 | −8.6 | −0.83 | −8.6 |
| 10. Benzoic acid | | −9.6 | −7.87 | −10.0 | −5.37$^c$ | −9.8 |
| 11. *p*-Chlorobenzoic | | −14.0 | −8.17 | −10.8 | −5.24$^c$ (?) | −10.4 |
| 12. *p*-Fluorobenzoic | | −12.5 | −7.97$^b$ | −10.6 | | −10.3 |
| 13. *p*-Methoxybenzoic | | −8.9 | −7.49 | −9.2 | −4.88$^c$ (?) | −9.3 |

[a] From ref 3. [b] From ref 8. [c] From ref 14. [d] This value was graciously provided by Professor Kebarle. Since it applies to the ionization process ($C_6H_5OH \rightarrow C_6H_5O^- + H^+$) it differs from the corresponding $\Delta H_i^{gas}$ value (346.9) by 7.9 kcal/mol ($T\Delta S°$) due to the increase in translational entropy as calculated through the Sakur–Tetrode equation.

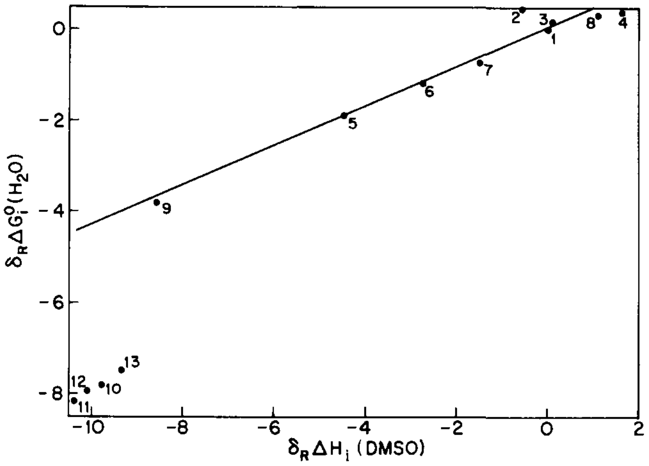

Figure 2. Relative free energies of ionization in water and in $Me_2SO$ for phenols and carboxylic acids. Numbers are as ordered in tables.

such processes in the gas phase are negligible so that $\delta\Delta G_i°(gas) \approx \delta\Delta H_i°(gas)$. In some cases changes of rotational symmetry numbers may lead to small entropy changes. However, for reactions such as those considered here, symmetry numbers are small and mostly cancel out. This assumption and the general validity of the gas-phase data for compounds of a structurally related series are strongly supported by the generally good agreement between McIver's ICR values,[25] obtained at 25 °C, and those of Yamdagni, McMahon, and Kebarle,[26] at 327 °C, using an entirely different method, i.e., high-pressure mass spectrometry.

McIver[25] found a good linear free-energy correlation between $\delta\Delta G_i°(H_2O)$ and $\delta\Delta G_i°$(gas) for a number of meta- and para-substituted phenols but none for ortho-substituted ones. He noted the similarity to protolysis of pyridines in water and the gas phase.[47] Another similar correlation of electron affinity in the gas phase and in THF was reported by Szwarc et al.[47] for resonance delocalized radical carbanions. In sharp contrast are the drastic differences between gas-phase and solution ionization properties for aliphatic alcohols[27,31,49] and aliphatic amines[50,51] where in each case the charge is tightly localized.

Kebarle's $\Delta G_i°$(gas) values[26] also correlate well with aqueous acidity values for phenols. Furthermore, his gas-phase acidities for benzoic acids correlate well with those in water. Substituent effects for phenols and for benzoic acids are much larger (five to ten times) in the gas phase than in solution. This degree of solvent leveling for oxygen acids is sharply in contrast to the modest attenuation factors for pyridinium ions[47] and delocalized carbonium ions[52] in water. We shall return to this matter later after calculating substituent effects on the solvation enthalpies of the oxyanions.

In view of the poor correlation between $\Delta G_i°(H_2O)$ and $\Delta H_i°(H_2O)$ for phenols, there is no reason to expect correlation of $\Delta H_i°$(gas) and $\Delta H_i°(H_2O)$ for these compounds. For benzoic acids $\Delta H_i°(H_2O)$ is so small[10] that its variation cannot be established with sufficient precision to test its proportionality to the gas-phase process.

We have found a remarkably good general correlation between enthalpies and free energies of ionization of many kinds of acids in $Me_2SO$.[28-30] This includes some of the phenols and benzoic acids in this report. We therefore feel justified in using it to estimate $\Delta G_i°(Me_2SO)$ values from measured $\Delta H_i°(Me_2SO)$. In Figure 2, $\Delta G_i°(H_2O)$ is plotted vs. $\Delta H_i°(Me_2SO)$ for phenols and benzoic acids.

A good linear free-energy (since $\Delta G_i°$ in $H_2O \propto \Delta H_i°$ in $Me_2SO$) relationship (slope = 0.74, $r$ = 0.963) is found for the phenols. The slope corresponds roughly to the ratio of dielectric constants for the two solvents 46.7/78.3 = 0.60. It appears as though the benzoic acids would generate a parallel line of similar slope, but the data are too few to tell definitely. In water the benzoic acids are somewhat less acidic relative to phenols than one would suppose from the acidities of the two classes of compounds in $Me_2SO$. In Figure 3, substituent effects on heats of ionization are compared with those in the gas phase. Again, as in Figure 2, separate and possibly parallel correlation lines seem to be generated for phenols and benzoic acids, with the latter again showing superior acidity. It is interesting to note from Table II that the acidity difference between phenol and benzoic acid is virtually the same in $Me_2SO$ as it is in the gas phase. In view of the fact that both phenols and carboxylic acids are capable of hydrogen bonding to both $H_2O$ and $Me_2SO$, and that both classes of anions can accept hydrogen bonds from water, it would be hard to interpret the solvent effect on their acidities in a rigorous manner from these data. Both Ritchie[52] and Bordwell[53] have commented authoritatively on the general question of acidities in these media. It is interesting in this context to note that Weiner[54] attempted to calculate the gas-phase acidities of a number of benzoic acids by an extensive factor analysis of p$K_a$'s in various solvents. Comparison of his predicted values with those subsequently found experimentally by Yamdagni, McMahon, and Kebarle[26]

**Table III.** Derived Heats of Transfer and Solvation for Acids and Their Anions

| AH | $\delta\Delta H_t{}^{Aa}$ | $\delta\Delta H_t{}^{B}$ | $\delta\Delta H_t{}^{C}$ | $\delta\Delta H_{S(AH)}{}^{D}$ | $\delta\Delta H_{S(A^-)}{}^{D}$ | $\delta\Delta H_{S(AH)}{}^{E}$ | $\delta\Delta H_{S(AH)}{}^{E}$ | $\lvert\delta\Delta\rvert H_{S(A^-)}{}^{Eb}$ | $\delta\Delta H_{S(A^-)}{}^{Ec}$ |
|---|---|---|---|---|---|---|---|---|---|
| 1. Phenol | 0<br>(−3.57 ± 0.12) | 0<br>(−6.97 ± 0.07) | 0<br>(−3.42) | 0<br>(−13.71) | 0 | 0<br>(−17.4) | 0<br>(−11.62) | 0 | 0 |
| 2. *o*-Cresol | −1.45 | −1.24 | 0.23 | −1.27 | −0.35 | −0.77 | −0.8 | −0.67 | −0.65 |
| 3. *m*-Cresol | 0.58 | 0.47 | −0.09 | −0.31 | −0.69 | −0.13 | 0.3 | −0.43 | −0.03 |
| 4. *p*-Cresol | 0.66 | 0.12 | −0.52 | −1.02 | −2.20 | −1.27 | 0.0 | −0.77 | −0.42 |
| 5. *o*-Chlorophenol | 1.94 | 0.56 | −1.36 |  |  |  | 0.3 |  | 2.16 |
| 6. *m*-Chlorophenol | 0.96 | −0.53 | −1.47 | 1.68 | 9.30 | 0.48 | −0.2 | 5.58 | 4.86 |
| 7. *p*-Chlorophenol | 0.65 | −0.74 | −1.37 | 5.13 | 10.88 | 4.03 | −0.4 | 9.18 | 4.75 |
| 8. *p-tert*-Butylphenol |  | 1.33 |  |  |  | 2.38 | 0.9 | 4.08 | 2.60 |
| 9. *p*-Nitrophenol | 0.77 | −2.35 | −3.10 | −4.24 | 17.9 | −7.07 | −1.6 | 10.67 | 15.67 |
| 10. Benzoic acid |  | 4.52 |  |  |  | −3.2 | 3.1 | −3.4 | 2.89 |
| 11. *p*-Chlorobenzoic acid |  | 6.15 |  |  |  | −0.9 | 4.2 | 2.7 | 7.83 |
| 12. *p*-Fluorobenzoic acid |  | 4.54 |  |  |  | −2.7 | 3.1 | −0.5 | 5.32 |
| 13. *p*-Methoxybenzoic acid |  | 7.99 |  |  |  |  | 5.5 |  | 5.12 |

[a] A, $CCl_4$-$H_2O$; B, $CCl_4$-$Me_2SO$; C, $Me_2SO$-$H_2O$; D, g-$H_2O$; E, g-$Me_2SO$. [b] Using $\Delta H°_{sub}$ values. [c] Using $\Delta H_t{}^{CCl_4\text{-}Me_2SO}$ values.

show many disparities. There seems to be no good substitute at this time for measuring gas-phase values.

For comparison with the parallel acidities of phenols and benzoic acids, we also show, in Figure 3, the well-known case of the aliphatic alcohols whose acidities in solution run opposite to their inherent acidities in the gas phase.

**Heats of Solvation from the Gas Phase.** In Table III we derive relative heats of transfer from $CCl_4$ to water and to $Me_2SO$ using data from Table I. Employing arguments set forth in the Results section, the relative heats of transfer from $CCl_4$ are used, in place of inaccessible or dubious heats of transfer from the gas phase. These are combined with heats of ionization in each solvent and in the gas phase to calculate the relative heats of solvation of both classes of anions to $Me_2SO$ and of phenoxide ions to water. We find that benzoic acids are too insoluble in water to permit measurement of their heats of solution.

Heats of transfer for phenols from $CCl_4$ to $Me_2SO$ are considerably more exothermic than those from $CCl_4$ to $H_2O$. This might be ascribed to the superior ability of $Me_2SO$ to accept hydrogen bonds[55] but in view of the peculiar effects of organic functions on heats of solution in water,[56,57] this interpretation is not convincing. The large endothermic relative heats of transfer for benzoic acids from $CCl_4$ to $Me_2SO$ suggest that they may be strongly associated in the former solvent. This is borne out by the data in Table I.

Heats of solvation relative to phenoxide ion, $\delta\Delta H_{(A^-)}{}^{g\text{-}Me_2SO}$ are shown in the last column of Table III. In view of the accumulated errors and assumptions used to derive these values, their "precision" is probably not better than ±2-3 kcal/mol. Nonetheless, the general trend of the numbers is reasonable mainly in terms of the effects of substituents on delocalization of charge from the phenoxide oxygen atom. Thus *p*-nitrophenoxide ion is much less exothermically solvated both in water and in $Me_2SO$ than is the unsubstituted phenoxide ion. The very large endothermic value here may seem anomalous when compared with Rochester's much lower indirect estimate.[22] Although we have some trepidation in presenting this value, we draw attention to the position of the point for *p*-nitrophenol in Figures 2 and 3, which suggests that it is probably no more than 5 kcal/mol out of line.

The low (endothermic) solvation enthalpies of the benzoate anions in $Me_2SO$ are consistent with the greater acidity of their conjugate acids. The values in the last column of Table III may also reflect some errors due to dimerization in $CCl_4$ (see the second column) and thus to a breakdown in our admittedly questionable method for estimating $\delta\Delta H_S{}^{g\text{-}Me_2SO}$ from $\delta\Delta H_S{}^{CCl_4\text{-}Me_2SO}$

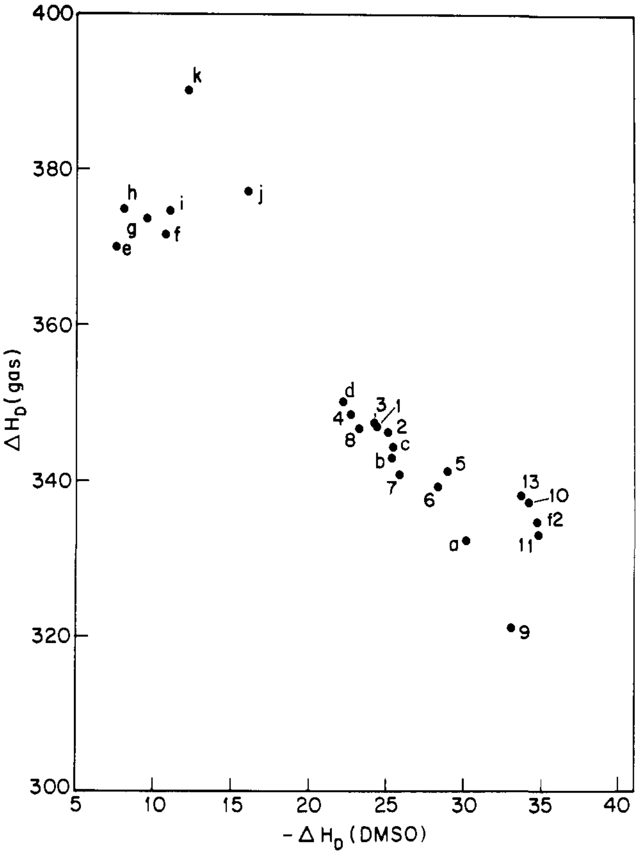

**Figure 3.** Heats of deprotonation of oxygen acids in $Me_2SO$ and gas phase. Numbers refer to phenols and benzoic acids; letters refer to as follows: (a) *p*-cyanophenol, (b) *m*-fluorophenol, (c) *p*-fluorophenol, (d) *p*-methoxyphenol, (e) di-*tert*-butylcarbinol, (f) neopentyl alcohol, (g) *tert*-butyl alcohol, (h) isopropyl alcohol, (i) ethanol, (j) methanol, (k) water.

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# Immobilized Radicals. 2. Hydrogen Bonding of the Semiquinone Anion Radical[1]

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**Abstract:** The ESR spectra of semiquinones in rigid alcohol solvents are broadened by radical-solvent interactions. These interactions are interpreted to be hydrogen bonds between the solvent's hydroxyl proton and the semiquinone's phenolate oxygen. Combined analysis of the change of the spectrum's line width and second moment as a function of the percentage of deuteration of the medium shows that one hydrogen bond occurs at each phenolate oxygen with a bond angle near 180°. Also shown by this analysis is the preference of hydrogen bonding of protons over deuterons in these systems.

It is customary in interpreting ESR spectra of organic radicals in solution to always consider the influence of solvent-radical interactions. These interactions manifest themselves as ion pairing, radical-solvent complex formation, secondary solvent radical production, hydrogen bonding, and polarity effects. All of these interactions affect the observed ESR spectrum, the magnitude of which can be as subtle as a small shift of the hyperfine splitting constants and the isotropic *g* factor or as pronounced as the incorporation of additional hyperfine splittings or even secondary radical signals. No matter what the magnitude of the effect, however, a radical's spectrum in the presence of these interactions will be different