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The Role of Hydrogen Bonding on the H-Atom-Donating Abilities of Catechols and Naphthalene Diols and on a Previously Overlooked Aspect of Their Infrared Spectra

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Abstract: Catechols and 1,8-naphthalene diols contain one "free" hydroxyl and one intramolecularly H-bonded hydroxyl group. The "free" hydroxyls are strong hydrogen-bond donors (HBDs) with α_2^H values (Abraham et al. *J. Chem. Soc., Perkin Trans. 2* **1989**, 699) ranging from 0.685 to 0.775, indicating that these compounds have similar HBD properties to those of strongly acidic phenols such as 4-chlorophenol ($\alpha_2^H = 0.670$) and 3, 5-dichlorophenol ($\alpha_2^H = 0.774$). Kinetic effects on H-atom abstractions from the diols in HB acceptor (HBA) solvents can be quantitatively accounted for over at least 50% of the available range of solvent HBA activities (as measured by their β_2^H values; see Abraham et al. *J. Chem. Soc. Perkin Trans. 2* **1990**, 521) on the basis of a single reactive OH group, the "free" OH. This free OH group is an outstanding H-atom donor in poor HBA solvents; e.g., in hexane rate constants for reaction with the DPPH• radical are 2.1×10^4 M^{-1} s^{-1} for 3,5-di-*tert*-butyl catechol and 2×10^6 M^{-1} s^{-1} for 4-methoxy-1,8-naphthalene diol, but only 7.4×10^3 M^{-1} s^{-1} for α-tocopherol (vitamin E). The diols are much more reactive than simple phenols because the O−H bond dissociation enthalpy of the "free" OH group is weakened by 5−9 kcal/mol by the intramolecular H-bond. The IR spectra of all the diols in CCl_4 show two fairly sharp O−H stretching bands of roughly equal intensity separated by 42−138 cm^{-1}. Addition of a low concentration of DMSO, a strong HBA, causes the band due to the intramolecularly H-bonded OH group to decrease in intensity to roughly half the extent that the "free" OH band loses intensity. The latter forms an intermolecular H-bond with the DMSO, the former does not. What has been overlooked in earlier work is that as the DMSO concentration is increased the band due to the intramolecularly H-bonded OH group first broadens and then evolves into a new, lower frequency (by 19−92 cm^{-1}) band. The magnitude of the shift in the frequency of the intramolecular OH band caused by H-bonding of HBAs to the "free" OH group, $\Delta\nu$, increases linearly as the HBA activity of the additive increases, e.g., for 3,5-di-*tert*-butylcatechol, $\Delta\nu/cm^{-1} = 33.8\ \beta_2^H$ ($R^2 = 0.986$). This may provide a new and simple method for determining β_2^H values.

Introduction

Rate constants for hydrogen atom abstraction by a radical, Y•, from a phenol, ArOH, depend on the intrinsic reactivities of the two reactants and the solvent in which the reaction occurs. The intrinsic reactivities are largely determined by the Y−H and ArO−H bond dissociation enthalpies (BDEs), since these determine the reaction enthalpies in the gas phase. Kinetic solvent effects (KSEs) arise largely from hydrogen-bond formation between ArOH and the solvent, S, in which ArOH is the hydrogen-bond donor (HBD) and S is the hydrogen-bond acceptor (HBA).[2−5] It is now well-established that intermolecularly hydrogen-bonded ArOH are essentially unreactive to all Y• (due to steric protection of the OH group by S) and that only "free", non-hydrogen-bonded ArOH react;[2−5] see Scheme 1. The concentration of free ArOH depends on the total [ArOH] and on the equilibrium constant, $K^S_{ArOH/S}$. The experimentally observed rate constant in solvent S, $k^S_{ArOH/Y\bullet}$, is therefore given by[2−5]

$$k^S_{ArOH/Y\bullet} = \frac{k^0_{ArOH/Y\bullet}}{1 + K^S_{ArOH/S}[S]} \qquad (I)$$

where $k^0_{ArOH/Y\bullet}$ is the rate constant for reaction of Y• with non-hydrogen-bonded ArOH and, hence, in the absence of other solvent effects, is also the experimental rate constant for reaction in a non-HBA solvent such as an alkane at concentrations of ArOH sufficiently low that there is no ArOH self-association via H-bonding.

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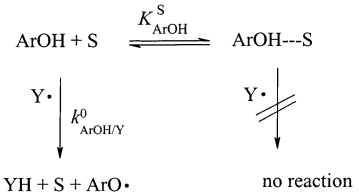
Scheme 1



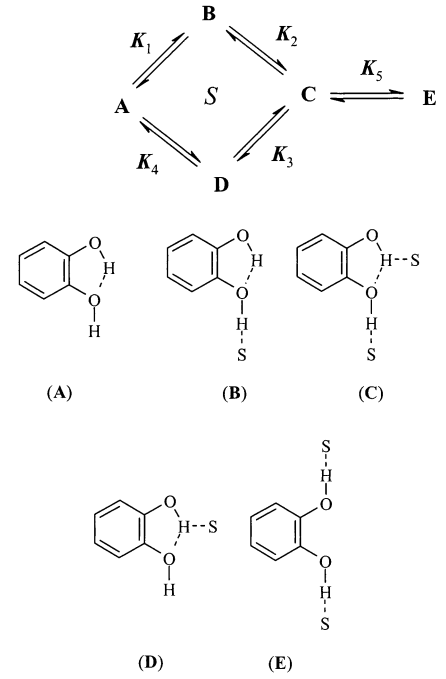
The enthalpy of the ArOH···S hydrogen bond (and hence the magnitude of $k^S_{ArOH/Y•}$) depends on two factors: first, the HBD ability of ArOH, which is most conveniently quantified (on a relative scale ranging from 0.00 to ca. 1.0) by Abraham et al.'s [6] extensive list of α_2^H values for HBDs, and, second, the HBA ability of S which, again, is most conveniently quantified (on a relative scale ranging from 0.00 to 1.00) by Abraham et al.'s[7] even more extensive list of β_2^H values for HBAs. The quantification of KSEs for reactions involving both highly reactive Y• (e.g., *tert*-alkoxyl) and relatively unreactive Y• (e.g., diphenylpicrylhydrazyl, DPPH•) using substrates and solvents having a wide range of α_2^H (0.26 to 0.73) and β_2^H (0.00 to 0.62) parameters, respectively, by a simple empirical equation, II, has been demonstrated[5] and confirmed.[8]

$$\log k^S_{ArOH/Y•} = \log k^0_{ArOH/Y•} - 8.3\alpha_2^H\beta_2^H \qquad \text{(II)}$$

KSEs for symmetrically substituted 1,3- and 1,4-dihydroxybenzenes are expected to follow eq II, because the two OH groups must have the same α_2^H. However, for 1,2-dihydroxybenzenes (catechols) and related compounds, $Ar(OH)_2$, which are capable of forming an intramolecular hydrogen-bond, the two hydroxyl groups are certainly not the same. Attention has recently focused on this class of compounds as potentially excellent peroxyl radical-trapping, chain-breaking antioxidants compared, for example, to hydroquinones.[9] This new attention has been aroused by two factors. First, theoretical calculations have shown that the intramolecular H-bond in the *o*-semiquinone radical is ca. 4 kcal/mol stronger than in the parent catechol.[10,11] As a consequence, the "free", i.e., non-H-bonded, hydroxyl group in catechol has a significantly lower O−H BDE than that for hydroquinone (leading to an increase in the intrinsic reactivities for H-atom donation by catechols relative to hydroquinones). It is also important to note that low O−H BDEs for the "free" OH group in catechols and related compounds have been unequivocally demonstrated experimentally.[12] Second, a large class of natural compounds present in many fruits and vegetables, the flavonoids, contains catechol moieties. The antioxidant (and antiatherogenic) properties of these polyphenols have been emphasized in several reviews.[13]

Despite the renewed interest in catechols as antioxidants, there have been only two studies of KSEs on H-atom abstraction from compounds containing a catechol moiety,[14,15] both of which were reported before eq II had been published.[5] In these studies the number of solvents examined was rather limited.[16] The validity, or otherwise, of eq II for a catechol is of interest because the hydrogen-bonding situation is, in principle, much more complex than that shown in Scheme 1 for a simple phenol; see Scheme 2.[17] There are three H-atom donors in Scheme 2, viz., **A**, **B**, and **D**, and KSEs could manifest themselves via the H-bonded structures **B**, **C**, **D**, and **E**.

Scheme 2



In view of the potentially complex nature of KSEs on catechols and related compounds and because of the simplicity of the experiments,[18] we chose 2,2-diphenyl-1-picrylhydrazyl (DPPH•) and 2,2-di(4-*tert*-octylphenyl)-1-picrylhydrazyl (DOPPH•) radicals (which show equal reactivities but very different solubilities in hexane) as the H-atom-abstracting agents. The rate constants for their reactions with compounds **1**−**4** (see Figure 1) were measured in up to seven solvents having β_2^H values ranging from 0.00 to 0.50 (i.e., half the maximum possible range from 0 to 1). It should be noted that two of these compounds have an intramolecular H-bond in a five-membered ring (viz. **1** and **2**) and the other two in a six-membered ring. The rates of reaction of DPPH• with catechol (**5**) and 2-methoxyphenol (**6**) were also measured in an alkane solvent.

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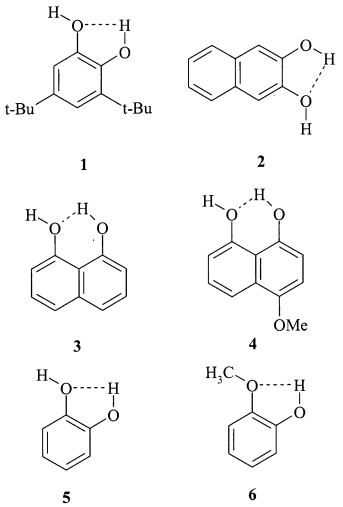
(16) Hexane, 1-propanol, *tert*-butyl alcohol, and acetone.[14] Cyclohexane and acetonitrile.[15]
(17) A kinetic analysis of H-atom abstraction from the species shown in Scheme 2 is given as Supporting Information.
(18) This simplicity is emphasized by the recent use of DPPH• to assess the stability of drug candidates toward reaction with oxygen and oxygen-centered radicals at an early stage in the drug development process; see: Karki, S. B.; Treemaneekarn, V.; Kaufman, M. J. *J. Pharm. Sci.* **2000**, *89*, 1518−1524.



1 2 3 4 5 6

Figure 1. Structures of diols **1**−**5** and phenol **6**.

Our kinetic measurements showed that log $k^{S}_{Ar(OH)_2/DPPH\bullet}$ was proportional to β_2^{H} (S) with no obvious "problems" arising from the presence of more than a single kinetically significant hydrogen-bonded complex (see Scheme 2). To check whether eq II applied to diols **1**−**4**, we had to measure their α_2^{H} values by standard methods using infrared spectroscopy.[5,6,8] During this IR work, we discovered that the frequency of the fundamental OH stretching vibration of the intramolecularly H-bonded OH group, ν_{OH}^{intra}, is not the same in **B** as it is in **A** (see Scheme 2). This observation is less surprising in itself than in the fact that it has been overlooked previously despite more than 50 years of IR work on H-bonding in phenols (including catechol, **5**!).

Results

Kinetic Solvent Effects on Ar(OH)$_2$/DPPH• Reactions. Experimental pseudo-first-order rate constants, k^{S}_{exptl}, were determined at 25 °C by monitoring the decay of the DPPH• absorption band at ca. 519 nm following the rapid mixing of equal volumes of deoxygenated stock solutions of DPPH• and the diol in the same solvent using a stopped-flow apparatus. Typically, the DPPH• concentration was in the range (1−9) × 10^{-5} M after mixing. The diol was generally used at five different concentrations covering about 1 order of magnitude in [Ar(OH)$_2$]. The diol concentrations were chosen so as to achieve a convenient reaction rate while using a large excess of diol to ensure pseudo-first-order conditions. Plots of k^{S}_{exptl} vs [Ar(OH)$_2$] were generally linear ($r^2 > 0.98$),[19,20] and their slopes gave the desired second-order rate constant in the chosen solvent, $k^{S}_{Ar(OH)_2/DPPH\bullet}$, according to eq III:

$$k^{S}_{exptl} = k^{S}_{0} + k^{S}_{Ar(OH)_2/DPPH\bullet}[Ar(OH)_2] \qquad (III)$$

The results are summarized in Table 1.[19] Figure 2 shows plots of log($k^{S}_{Ar(OH)_2/DPPH\bullet}$/M^{-1} s^{-1}) vs β_2^{H} (S) that are (perhaps surprisingly; see Scheme 2) linear and can be described by eq IV

$$\log k^{S}_{Ar(OH)_2/DPPH\bullet} = \log k^{0}_{Ar(OH)_2/DPPH\bullet} - A\beta_2^{H} \qquad (IV)$$

where $k^{0}_{Ar(OH)_2/DPPH\bullet}$ is the intercept and corresponds to the rate constant in a solvent having $\beta_2^{H} = 0.00$ (such as an alkane). Values of $k^{0}_{Ar(OH)_2/DPPH\bullet}$ and A are summarized in Table 2.

There would appear to be no published values of α_2^{H} for catechol or any related diol.[21] Moreover, by combining eqs II and IV we obtain KSE-derived α_2^{H} values via the relationship

$$\alpha_2^{H}(KSE) = A/8.3 \qquad (V)$$

These α_2^{H}(KSE) values are included in Table 2.

Table 1. Rate Constants ($10^{-2}k^{S}_{Ar(OH)_2/DPPH\bullet}$/M^{-1} s^{-1}) for H-Atom Abstraction from Diols **1**−**4** by DPPH• in Various Solvents at 25 °C

solvent	β_2^{H} [a]	**1** [b]	**2**	**3**	**4**
hexane[c]	0.00	210 (200)	13	3100	20000
1-chlorobutane	0.15	14	1.1	150	900
acetonitrile	0.44	0.64[d]	0.20	*d*	
ethyl acetate	0.45	0.52	0.15	1.6	130
n-propanol	0.45	0.70 (0.80)			
tert-butyl alcohol	0.49	0.44 (0.56)		3.5	
acetone	0.50	0.12 (0.17)	0.11	*d*	

[a] From ref 7. [b] Rate constants in parentheses are from ref 14 at 30 °C. [c] DOPPH• in hexane only. [d] See footnote 20.

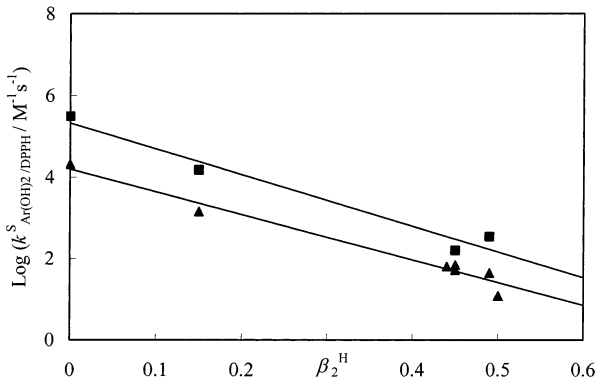


Figure 2. Plots of log($k^{S}_{Ar(OH)_2/DPPH\bullet}$/M^{-1} s^{-1}) vs β_2^{H}(S) for **1** (▲) and **3** (■). The linear best-fit equations are, respectively, log($k^{S}_{Ar(OH)_2/DPPH\bullet}$/M^{-1} s^{-1}) = 4.20−5.58 × β_2^{H}(S) (R^2 = 0.97) and log($k^{S}_{Ar(OH)_2/DPPH\bullet}$/M^{-1} s^{-1}) = 5.33−6.33 × β_2^{H}(S) (R^2 = 0.96).

Table 2. Summary of Substrate/DPPH• KSE Data (eq IV), α_2^{H}(KSE) (eq V), IR-Determined Values of K^{i} for 1:1 Complex Formation with DMSO in CCl_4 at Ambient Temperatures (eq VI), Derived α_2^{H}(IR) Values (eqs VII and VIII), and Other Data

substrate	$10^{-3}k^{0}$/M^{-1} s^{-1}	*A* (eq. IV)	α_2^{H}(KSE) (eq V)	K^{i}/M^{-1} (eq VI)	α_2^{H}(IR) (eqs VII and VIII)
1	21	5.6	0.67	695	0.685
2	1.3	7.0[a]	0.84	1547	0.746
3	310	6.3	0.76	2264	0.775
4	2000			1500	0.744
5	1.8[b]			1190	0.726
6	7×10^{-4} [b,c]	2.0[d]	0.24[d]	2.5[e]	0.26[e]

[a] Based on kinetic measurements in hexane and 1-chlorobutane only. [b] The only kinetic measurement was in an alkane solvent. [c] Based on initial rates, because the high O−H BDE (86.6 kcal/mol)[25] makes the reaction with DPPH• much more noticeably reversible than is the case for the diols and most phenols. The reverse reaction was estimated to have a rate constant of ca. 10^5 M^{-1}s^{-1}. [d] Based on a fairly extensive KSE study using *tert*-alkoxyl radicals; see ref 26. [e] Reference 6.

(19) Full data are given as Supporting Information.

(20) With the following exceptions: (i) **1** in CH_3CN, for which k^{S}_{exptl} vs [**1**] gave an excellent linear correlation at low [**1**] (which was used to determine $k_{1/DPPH}^{CH3CN}$), but at high [**1**], k^{S}_{exptl} was somewhat greater than expected (possibly because **1** self-associates to give more reactive dimers or oligomers); (ii) **3** and **4** in CH_3CN and $(CH_3)_2CO$ for which k^{S}_{exptl} increased with [Ar(OH)$_2$] to a maximum and then declined as [Ar(OH)$_2$] was further increased. These data could not be used to obtain the desired second-order rate constants. The origin of these kinetic peculiarities was not pursued, since measurements could be made in ethyl acetate, another good HBA solvent. However, it was shown by ^{1}H NMR that **3** and **4** did not react directly with CD_3CN or $(CD_3)_2CO$.

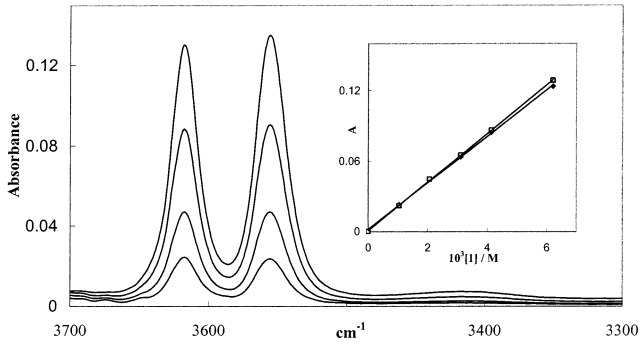


Figure 3. Fundamental OH stretching region in the IR spectrum of 3,5-di-*tert*-butylcatechol (**1**) at [**1**] = 1.0, 2.1, 4.1, and 6.2 mM. Inset: Absorbance as a function of [**1**] for the "free" OH (◆) and intramolecularly H-bonded OH (□) bands.

Values of α_2^H Derived from Infrared Spectroscopy. Since the diol/DPPH• KSE data correlate linearly with β_2^H(S) (i.e., they fit eq IV) it would appear that only one kinetically significant hydrogen-bonded complex needs to be invoked to quantify these reactions over the explored range of solvent HBA activities (β_2^H from 0.0 to 0.5, or slightly less; Table 1). That is, KSEs for the diols are adequately described by Scheme 1 and it is not necessary to resort to the (presumably) true situation shown in Scheme 2 with its four hydrogen-bonded complexes. To explore further the simplicity of the (effective) interaction between diols and HBA solvents and to check the reliability of α_2^H(KSE) values derived from Scheme 1, we turned to infrared spectroscopy. Values of α_2^H for hydroxylic substrates, ROH, are normally determined by monitoring the O−H fundamental stretching region of the IR spectrum in CCl_4 at ambient temperatures.[6] Dilute solutions of ROH (no self-association) are used. The equilibrium constant, K^i, for 1:1 complex formation with an added, "calibrated"[6] base are determined from the HBA-induced decrease in the intensity of the free OH band by a least-squares fitting of the nominator vs denominator in eq VI

$$K^i = \frac{[\mathrm{ROH}\cdots\mathrm{HBA}]_{\mathrm{H-bonded}}}{[\mathrm{ROH}]_{\mathrm{free}}[\mathrm{HBA}]_{\mathrm{free}}} \qquad \text{(VI)}$$

Values of α_2^H are then calculated using the relationships[6] given by eqs VII and VIII, where L_{HBA} and D_{HBA} are constants that are known for a calibrated base.

$$\log K^i = L_{\mathrm{HBA}} \log K_A{}^H + D_{\mathrm{HBA}} \qquad \text{(VII)}$$

$$\alpha_2{}^H = (\log K_A{}^H + 1.1)/4.636 \qquad \text{(VIII)}$$

In CCl_4 the IR spectra of catechol and the other diols show two fairly sharp OH fundamental stretching bands of roughly similar intensity; e.g., for **1**, see Figure 3. The slightly narrower and slightly less intense band at the higher wavelength (e.g., 3617.7 cm^{-1} for **1**) is due to the free OH group and the slightly broader band at the lower wavelength (e.g., 3555.8 cm^{-1} for **1**) is due to the intramolecularly H-bonded OH group. For all the diols, **1**−**5**, this pair of bands obey the Lambert−Beer law, i.e., their intensities increased linearly with increasing diol concentration in the range 0.4−6 mM, which indicates that there is no

(21) There is, however, an "overall", or "summation" hydrogen bond acidity for cathechol, $\sum \alpha_2^H = 0.85$ (cf. Table 2); see: Abraham, M. H.; Chadha, H. S.; Whiting, G. S.; Mitchell, R. C. *J. Pharm. Sci.* **1994**, *83*, 1085−1100.

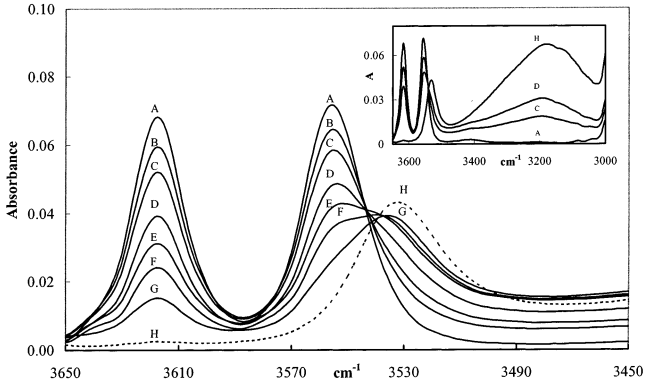


Figure 4. IR spectra of 3.3 mM **1** in CCl_4 containing different concentrations of DMSO. Spectrum, [DMSO]/mM: A, 0; B, 0.78; C, 1.6; D, 3.1; E, 4.7; F, 6.2; G, 12.5; H, 94.

self-association of any of the diols at these concentrations in CCl_4 (for **1** see Figure 3 and for the other diols see Supporting Information). We used DMSO, a very strong HBA ($\beta_2^H = 0.78$), as our calibrated base ($L_{DMSO} = 1.2399$, $D_{DMSO} = 0.2656$).[6] Upon the addition of low concentrations of DMSO to the diols in CCl_4, the bands due to the free OH group and the intramolecularly H-bonded OH group both decrease in intensity (for **1**, see Figure 4) and a new, broad, and intense band due to the formation of an intermolecular H-bond appears at a much lower frequency, e.g., ca. 3190 cm^{-1} for **1**; see inset in Figure 4.

DMSO added at concentrations in the range 0.8 to ca. 3.1 mM decreased the intensity of the band due to the free OH group of **1** to about twice the extent as the same [DMSO] reduced the intensity of the band due to the intramolecularly H-bonded OH group (see Figure 4). This was not expected, because reasonable models for the HBD behavior of the free OH and intramolecularly H-bonded OH groups in catechol would seem to be the similarly electron-rich free OH group in 4-methoxyphenol and the intramolecularly H-bonded OH group in 2-methoxyphenol (**6**) or 2,6-dimethoxyphenol (**7**), respectively, yet the α_2^H value for 4-methoxyphenol is 0.55[5] and for **6** it is 0.26.[5,6] Using eqs VII and VIII with the known values of *L* and *D* for DMSO (*vide supra*) the equilibrium constants for 1:1 complex formation with DMSO, K^i, can be calculated to be 116 M^{-1} for 4-methoxyphenol but only 2.5 M^{-1} for **6**. Thus, the intensity of the free OH band in (for example) **1** would be expected to decrease upon the addition of DMSO about (116/2.5=) 46 times as rapidly as the decrease in the intensity of the intramolecularly H-bonded OH band of **1**, *not* twice as rapidly. In agreement with these expectations, although the intensity of the intramolecularly H-bonded OH band in **1** is reduced by about one-third by the addition of ca. 3 mM DMSO (Figure 4), a similar one-third decrease in the intensity of the intramolecularly H-bonded OH band in **6** requires ca. 200 mM DMSO (Figure 5). [The abilities of DMSO to reduce the intensity of the OH band in **6** and **7** are similar and the new intermolecular H-bonded OH bands that grow in (Figure 5) are as well-defined as is the case for **1** (see inset in Figure 4, and for "ordinary" meta- and para-substituted phenols) and occur at rather similar frequencies, viz., ca. 3200 cm^{-1} for **1** and **6** H-bonded to DMSO[22].]

A further small increase in the concentration of DMSO added to the solution of **1** in CCl_4 (from 3.1 to 4.7 mM and then to 6.2 mM) provided the explanation for the apparently different HBD abilities of the intramolecularly H-bonded OH group in

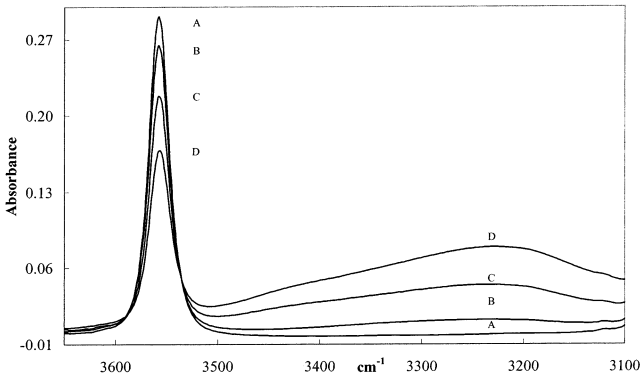


Figure 5. IR spectra of 14.5 mM **6** in CCl_4 containing different concentrations of DMSO. Spectrum, [DMSO]/mM: A, 0; B, 22; C, 93; D, 202.

the diols and in 2-methoxyphenol. In the diols, the addition of DMSO induces a broadening of the intramolecular H-bonded OH band (see Figure 4), which does not occur in the *o*-methoxyphenols (see Figure 5). This is due to a second band that grows in at ca. 3535 cm^{-1} for **1**, first as a "shoulder" to the 3555.8 cm^{-1} band and then as a distinct band. There is a fairly clean isobestic point[23] (3543 cm^{-1}), which indicates that the addition of DMSO converts the species responsible for the 3555.8 cm^{-1} band directly and without an intermediate into a new species. At [DMSO] $\approx$ 94 mM, this new species yields a reasonably "clean" band[24] at 3530 cm^{-1} with the complete disappearance of the 3555.8 cm^{-1} band (see spectrum G and H in Figure 4). At the highest concentration of [DMSO] there is extensive intermolecular H-bonding that probably includes at least some H-bonding to the intramolecularly H-bonded hydrogen atom as shown in structure **C** of Scheme 2 (see spectrum H in the inset of Figure 4). The formation of intermolecular H-bonds to intramolecularly H-bonded OH groups in 2-methoxyphenol[22] and other *o*-methoxyphenols have previously been demonstrated both by measurements of O−H BDEs[25] and by measurements of KSEs on rates of H-atom abstraction.[26]

On the basis of the above analysis of the effects of HBAs on the IR spectra of dilute solutions of the diols in CCl_4, we have used the DMSO-induced decrease in the intensity of the "free" OH band to determine K^i and hence, via eqs VII and VIII, the value of α_2^H for their "free" hydroxyl groups.[27] These values are given in Table 2. The diols most relevant IR parameters, viz., fundamental OH-stretching frequencies (ν_{OH}), extinction coefficients (ϵ), and bandwidths at half-height ($\Delta\nu_{1/2}$) are summarized in Table 3.

(22) Interestingly, DFT calculations on **6**/HBA complexes have revealed that the O−H stretching frequencies for the intermolecular hydrogen-bonded complexes are almost identical for the "HO-away-from-MeO" conformer, i.e., the simple intermolecular H-bond, as for the "HO-toward-MeO" conformer, i.e., the trifurcated inter−intra hydrogen bond; see footnote 34 in ref 11.

(23) Small, random shifts in the apparent isosbestic point (Figure 4) probably arise because the overlapped spectra were obtained using different solutions of **1** in CCl_4 and small differences in the true concentration of **1** are not unlikely. The same is true for the other diols; see the Supporting Information.

(24) The 3530 m^{-1} band sits on the "tail" of the broad, intense 3190 m^{-1} band arising from intermolecular H-bonds between **1** and DMSO; see the inset in Figure 4.

(25) de Heer, M. I.; Korth, H.-G.; Mulder, P. *J. Org. Chem.* **1999**, *64*, 6969−6975.

(26) de Heer, M. I.; Mulder, P.; Korth, H.-G.; Ingold, K. U.; Lusztyk, J. *J. Am. Chem. Soc.* **2000**, *122*, 2355−2360.

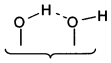
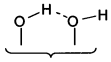
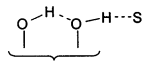
(27) There can be only one "free" OH at any particular time for **2**, **3**, **5**, and **6** for reasons of symmetry. For **1** the principle "free" OH is as shown in Figure 1, because an OH group pointing "toward" an *o-tert*-butyl group is disfavored for steric reasons by ca. 1.6 kcal/mol[28] relative to the same OH pointing "away". In the case of **4**, the preferred "free" OH and its degree of preference is unknown.

Discussion

KSEs on H-atom abstraction by DPPH• from diols **1**−**4** and the effects of DMSO on their fundamental OH stretching bands are fully self-consistent. This is indicated, particularly, by the similarity in the α_2^H(KSE) and α_2^H(IR) values; see Table 2. These diols form intermolecular H-bonds with added HBAs using their "free" OH group essentially exclusively. Thus, under most experimental conditions, only structures **A** and **B**, from Scheme 2, are required to explain the effects of HBA solvents on the kinetic responses of catechols and the effects of HBA solutes on their IR spectroscopic responses. Two related structures would, of course, describe the responses of the 1,8-naphthalene diols. Over the experimental range of solvent β_2^H values (0.0 to a maximum of 0.50), the KSEs on **1**−**4** are adequately represented by Scheme 1 and are well-described by eq II. This is because the "free" OH is (i) much more reactive than the intramolecularly H-bonded OH and (ii) a very much stronger HBD than the intramolecularly H-bonded OH. Kinetically, these two statements are well-illustrated by (i) the fact that in an alkane solvent catechol (**5**) with its free OH group is more than 3 orders of magnitude more reactive toward DPPH• than 2-methoxyphenol (**6**) with its intramolecular H-bonded OH (see Table 2) and (ii) the fact that α_2^H values for catechol and the other diols (range by IR 0.685−0.775) are all very much greater than for 2-methoxyphenol (0.26) (see Table 2) and are, in fact, comparable to α_2^H values for such strongly acidic phenols as 4-chlorophenol ($\alpha_2^H = 0.670$)[5] and 3,5-dichlorophenol ($\alpha_2^H = 0.774$).[5] Interestingly, and as might have been expected, a comparison of α_2^H values for the three diols that do not have other electron-donating substituents reveals that these values are significantly smaller for the two compounds that form the weaker five-membered intramolecular H-bonded rings, viz. **2** ($\alpha_2^H = 0.746$) and **5** ($\alpha_2^H = 0.726$), than for the compound that forms the stronger six-membered intramolecular H-bonded ring, **3** ($\alpha_2^H = 0.775$).

In the non-HBA solvent, hexane, all the diols are much more reactive toward DPPH• than is phenol, e.g., $k^0/M^{-1}\,s^{-1} = 0.16$,[5] 1.8×10^3, 2.1×10^4, and 2×10^6 for phenol, catechol, 3,5-di-*tert* butylcatechol, and 4-methoxy-1,8-naphthalenediol, respectively. Indeed, most of these diols are more reactive toward DPPH• than nature's favored phenolic antioxidant, α-tocopherol (vitamin E), for which $k^0 = 7.4 \times 10^3\ M^{-1}\,s^{-1}$.[5] The excellent fits to eq II from $\beta_2^H = 0.0-0.5$ should not blind us to the fact that this relationship can be calculated to break down in HBA solvents having very high β_2^H values. For example, if we assume that the intramolecularly H-bonded OH group in catechol (**5**) is adequately modeled by the OH group in 2-methoxyphenol (**6**, $k^0 = 0.7\ M^{-1}\,s^{-1}$, $\alpha_2^H = 0.26$;[6] see Table 2), then the rate constant for its reaction with DPPH• in acetone ($\beta_2^H = 0.50$) can be calculated (via eq II) to be $5.84 \times 10^{-2}\ M^{-1}\,s^{-1}$. The "free" OH group in **5** has $k^0 = 1.8 \times 10^3\ M^{-1}\,s^{-1}$ and $\alpha_2^H = 0.73$ (Table 2), and hence, the calculated rate constant for reaction of this OH group with DPPH• in acetone is $1.68\ M^{-1}\,s^{-1}$. Thus, the intramolecularly H-bonded OH group in **5** should contribute only $5.8 \times 10^{-2}/(1.68 + 0.058) = 3.3\%$ to the measured overall rate constant in acetone. However, in HMPA ($\beta_2^H = 1.00$) the calculated rate constant for reaction of the intramolecular H-bonded OH group and "free" OH group of **5**

Table 3. Fundamental OH Stretching Frequencies (ν/cm^{-1}), Bandwidths at Half Heights ($\Delta\nu_{1/2}$/cm^{-1}), and Extinction Coefficients ($\epsilon \times l$/M^{-1}, where l = path length ≈ 1 mm) for Diols **1**−**5** and Phenols **6** and **7** in Carbon Tetrachloride without and with Low Concentrations of DMSO

Structure type	IR Parameters	**1**	**2**[b]	**3**[b]	**4**[b]	**5**[b]	**6**	**7**
		Free OH Group						
A 	υ^{free}(**A**)[a]	3617.7	3608.4	3598.1	3601.7	3615.0		
	$\Delta\upsilon_{1/2}$	22.9	25.8	28.1	26.1	23.8		
	$\epsilon \times l$	20.3	23.5	20.0	16.3	24.3		
	Intramolecularly H-bonded OH Group (with Free OH Group)							
A 	υ^{intra}(**A**)[d]	3555.8	3566.5	3477.1	3463.9	3569.6	3557.6	3553.8
	$\Delta\upsilon_{1/2}$	26.0	27.0	40.0	54.0	25.5	28.0	25.0
	$\epsilon \times l$	21.0	29.0	19.0	11.0	23.5	20.1	20.6
	Intramolecularly H-Bonded OH Group (with Other OH Group H-Bonded to DMSO)							
B[c] 	υ^{intra}(**B**)[d]	3530	3542	3385	3300[e]	3551		
	$\Delta\upsilon_{1/2}$	28[f]	28[f]	80	ca. 100	33[f]		
	$\epsilon \times l$	11[f]	18[f]	9	ca. 20	11.5[f]		
A/B[g]	$\Delta\upsilon^{intra}$(**A** - **B**)	26	25	92	ca. 64	19		
A / B[h]	υ_{isosb}(**A** / **B**)	3543	3551	3436	ca. 3430	3558		

[a] Errors are generally ±0.2 cm^{-1}. [b] To improve solubility, the CCl_4 contained CH_2Cl_2 in the following volume %: **2**, 2.4%; **3** and **4**, 4.8%; **5**, 0.3%. [c] S in this structure represents DMSO. [d] Errors are generally ±1 cm^{-1}. [e] Error > ±1 cm^{-1}, because this band is broad and poorly resolved relative to other bands of this type. [f] Optimized value estimated by computer simulation. [g] DMSO-induced shift in frequency for the intramolecularly bonded OH group. [h] Isobestic point as the intramolecular H-bonded OH group in **A** changes to the intramolecular H-bonded OH group in **B**.

are 4.8 × 10^{-3} and 1.5 × 10^{-3} M^{-1} s^{-1}, respectively. Thus, in HMPA, ca. 75% of the **5**/DPPH• reaction will involve the intramolecularly H-bonded OH group. The two hydroxyl groups in catechol can be calculated to be equally reactive toward DPPH• in a solvent having $\beta_2^H = 0.87$, and a plot of log $k^s_{5/DPPH•}$ vs β_2^H would be expected to show a sharp decrease in slope at this point (from −8.3 × 0.73 = −6.06 to −8.3 × 0.26 = −2.16).

The other main point of kinetic interest is that the parent 1,8-naphthalenediol (**3**) is more than 2 orders of magnitude more reactive toward DPPH• in alkane solvents than the parent catechol (**5**) (see Table 2). This means that the O−H BDE of the free O−H group in **3** must be considerably weaker than that of the free O−H group in **5**. A part of this reactivity difference can be attributed to the same factors that make 1-naphthol a better H-atom donor than phenol.[29] However, DFT calculations indicate that there is another important factor contributing to the higher reactivity of **3** relative to **5**. This is the difference in the strengths of the intramolecular H-bond in the diol relative to its radical. Thus, the intramolecular H-bond enthalpies have been calculated[9] to be 6.2 and 14.8 kcal/mol for **3** and **3**• (difference, 8.6 kcal/mol) and to be 3.8 and 9.1 kcal/mol for **5** and **5**• (difference, 5.3 kcal/mol). The intramolecular H-bond therefore provides a much greater driving force for H-atom abstraction in **3** (with its six-membered H-bond ring) than in **5** (with its five-membered H-bond ring).

It is well-known that the addition of electron-donating groups (EDGs) to the aromatic ring of phenol lowers the O−H BDE and hence increases the H-atom-donating ability of EDG-substituted phenols. This effect accounts for the greater reactivity of 3,5-di-*tert*-butylcatechol (**1**) relative to catechol (**5**) and of 4-methoxy-1,8-naphthalenediol (**4**) relative to 1,8-naphthalenediol (**3**). The similar reactivities of **5** and 2,3-naphthalenediol were somewhat surprising. However, this similarity is consistent with the fact that 2-naphthol is a poor H-atom donor relative to 1-naphthol.[29a,d]

The effect of HBAs on the IR spectrum of only one of the diols studied in the present work appears to have been reported.[30,31] This was catechol (**5**). With DMSO as the HBA in CCl_4 as solvent, Spencer et al.[31] give K^i for the 1:1 (**5**/DMSO) complex as 326 M^{-1} at 20 °C and 260 M^{-1} at 25 °C, values which are in poor agreement with our measurement of K^i for the same 1:1 complex, viz., 1190 M^{-1}, at ambient temperature (see Table 2). The 1:1 (**5**/DMSO) complex was assigned[31] structure **B** (Scheme 2), which is the same as our own IR- and KSE-based structural assignment for the 1:1 complex. Unfortunately, there is a further disagreement, because Spencer et al. went on to claim that a second intermolecular H-bonded species was formed, and not just with the strong HBA DMSO[31] ($\beta_2^H = 0.78$), but also with three much weaker HBAs, THF[31] ($\beta_2^H = 0.51$), diethyl ether[30] ($\beta_2^H = 0.45$), and *n*-Bu_2S[31] ($\beta_2^H = 0.29$). These second species were assigned to 1:2 (**5**/HBA) complexes and were given a structure roughly corresponding to **E** in Scheme 2. Spencer et al. incorrectly interpreted their observation that even low concentrations of the added HBA decreased the "molar absorptivity" (peak height) of the band due to the "free" OH as well as that due to the intramolecular H-bonded OH (see Figures 4 and Supporting Information). No spectra were given in these papers and the HBA-induced "broadening" of the band due to the intramolecular H-bonded OH group and its eventual 19 cm^{-1} shift to lower frequencies (Table 3) must have been overlooked.[32] This is surprising,

(28) Ingold, K. U.; Taylor, D. R. *Can. J. Chem.* **1961**, *39*, 471−480. Ingold, K. U.; Taylor, D. R. *Can J. Chem* **1961**, *39* 481−487. Ingold, K. U. *Can J. Chem.* **1962**, *40*, 111−121.
(29) (a) For example, the *tert*-butylperoxyl radical at 30 °C, k(phenol) = 2.8 × 10^3 M^{-1} s^{-1} [29b] and k(1-naphthol) = 1.5 × 10^5 M^{-1} s^{-1} (extrapolated from lower temperatures).[29c] (b) Chenier, J. H. B.; Furimsky, E.; Howard, J. A. *Can. J. Chem.* **1974**, *52*, 3682−3677. (c) Howard, J. A.; Furimsky, E. *Can J. Chem.* **1973**, *51*, 3738−3745. (d) For *tert*-butylperoxyl (extrapolated to 30 °C) k(2-naphthol) = 3.3 × 10^4 M^{-1} s^{-1}.[29b]
(30) Spencer, J. N.; Heckman, R. A.; Harner, R. S.; Shoop, S. L.; Robertson, K. S. *J. Phys. Chem.* **1973**, *77*, 3103−3106.
(31) Spencer, J. N.; Robertson, K. S.; Quick, E. E. *J. Phys. Chem.* **1974**, *78*, 2236−2240.

because Spencer at al.'s[31] own results forced them to try to explain two embarrassing facts. First, the equilibrium constants, K_2, for the **B** + HBA ⇌ **B**/HBA (i.e., **E**), a 1:2 complex, had to be substantially greater than the corresponding equilibrium constant, K^i, for the **A** + HBA ⇌ **B**, a 1:1 complex. Second, they observed that the intramolecularly H-bonded OH group in 2-methoxyphenol behaved in a completely different manner toward added HBAs than did the intramolecularly H-bonded OH group in catechol; e.g.,[31] "No change in the molar absorptive of this band... was detected and no additional absorbance bands were found in solutions containing THF or *n*-Bu_2S indicating that the intramolecular bond in (2-methoxyphenol) persists at the electron donor (HBA) concentrations used in this work". Convoluted entropic arguments were employed to explain away these two unwelcome facts.

Fortunately, and as we have shown, entropic arguments are not required to explain the IR spectra. Indeed, it would be astonishing if the intramolecular H-bonded OH stretching frequency were to be the same in a non-intermolecularly H-bonded diol, i.e., **A** (Scheme 2), as in the corresponding intermolecularly H-bonded complex, **B**. The occurrence of an isosbestic point for each diol upon the addition of DMSO indicates a smooth transition from **A** to **B** with no other intermediates; i.e., [**A**] + [**B**] is constant, which rules out a contribution from **C** (see Scheme 2). At high [DMSO] there is probably some **C** present (*vide supra*). The shift of the intramolecularly H-bonded band to lower frequencies with diols **1-5** (a shift of 19 to 92 cm^{-1}, see Table 3) indicates that there is a decrease in the strength of the OH bond in the intramolecularly H-bonded OH group in **B** relative to **A**, as would be expected. That is, formation of the intermolecular H-bond in **B** will produce a net flow of electrons through the O−H···O−H···S system from the first O−H toward the S, thus reducing the electron density in the first OH bond and, hence, weakening this bond. In other words, the O−H BDE of the intramolecular H-bonded OH group will be weakened and the intramolecular H-bond will be strengthened by the formation of an intermolecular H-bond between the "free" OH group and S. The stronger the OH···S intermolecular H-bond, the greater should be the net electron flow from the first O−H toward S and, hence, the greater should be the weakening of the OH bond of the intramolecularly H-bonded OH group and the greater should be the frequency shift $\Delta\nu$(**A**−**B**).

We chose to explore this phenomenon in more detail using diol **1** and solvents having the maximum possible range of HBA activities (β_2^H values). The results are summarized in Table 4, and the frequency shift of the intramolecular H-bonded OH group, $\Delta\nu$(**A**−**B**), has been plotted against β_2^H in Figure 6. A rather good linear correlation is obtained:

$$\Delta\nu(\mathbf{A}-\mathbf{B})/\mathrm{cm}^{-1} = 33.8\beta_2^{\mathrm{H}} \quad (r^2 = 0.986)$$

While further work in this area with the other diols and with a more varied range of HBAs is required, the present preliminary results suggest that the shift in frequency of the intramolecularly H-bonded OH group of suitable diols in CCl_4 induced by low concentrations of additives might be a quick and simple method for estimating β_2^H values, because the concentration of additive does not need to be determined.

(32) Indeed, to quote Spencer et al.[31] regarding any shift of this band to lower frequencies: "No such shift is observed".

Table 4. Shift in the Frequency of the Intramolecularly H-bonded OH Group in 3,5-Di-*tert*-butylcatechol (**1**) in CCl_4 Caused by the Intermolecular H-bond between the "Free" OH Group (structure **A**) and a Low Concentrations of an Added HBA (structure **B**)

HBA	$\beta_2^{H\,b}$	ν_{intra}(**B**)/$cm^{-1\,b}$	$\Delta\nu$(**A**–**B**)/$cm^{-1\,b}$
CCl_4	0.00	(3555.8)[c]	0.0
mesitylene	0.20	3548.9	6.9
ethyl acetate	0.45	3543.3	12.5
acetone	0.50	3536.8	19.0
THF	0.51	3537.8	18.0
DMF	0.66	3530.9	24.9
DMSO	0.78	3530.0	25.8
HMPA	1.00	3523.5	32.3

[a] From ref 7. [b] Error ±1 cm^{-1}. [c] Structure **A**.

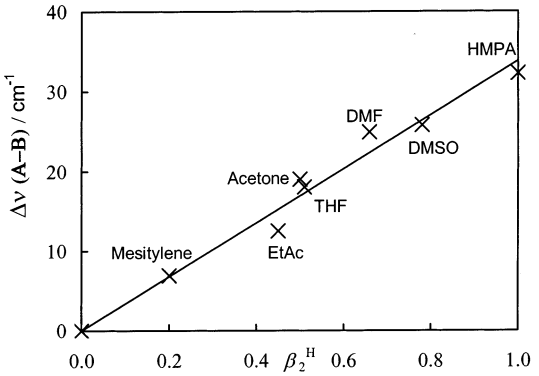


Figure 6. Change in frequency for the intramolecularly H-bonded OH group of **1** induced by additives having the maximum range HBA activities possible.

Experimental Section

Materials and Instruments. Phenols were purchased from Aldrich, except **3** and **4**, which were synthesized according to procedures reported previously.[9] All phenols were recrystallized from hexane/ethanol prior use except for **4**, which is unstable in air. 2,2-Diphenyl-1-picrylhydrazyl (DPPH•) was purchased from Aldrich and 2,2-di(4-*tert*-octylphenyl)-1-picrylhydrazyl (DOPPH•) from Northern Sources, Inc., Houghton, MI. Both were used as received. All solvents used in the kinetics were of analytical grade and were distilled before use. The carbon tetrachloride used in the IR measurements was "for IR-Spectroscopy" from Fluka and was used as received. The decay of DPPH• or DOPPH• in the presence of known concentrations of phenols **1**−**6** was recorded on an Applied Photophysics stopped-flow spectrophotometer (SX 18 MV) equipped with a 150 W xenon arc lamp or using an Applied Photophysics RX-1000 stopped-flow attachment to a Varian Cary 100 spectrophotometer. The IR measurements were made with a CaF_2 or KBr cell on a Mattson Genesis II FT-IR or Perkin-Elmer BX FT-IR spectrometer system.

Measurement of Rate Constants for the Reaction of Ar(OH)$_2$ with DPPH• or DOPPH• in Various Solvents. There was no observable difference in the reactivities of DPPH• and DOPPH•. However, for solubility reasons, DOPPH• was generally used in hexane, whereas DPPH• was generally used in the polar solvents. The procedure used to determine $k^S_{Ar(OH)_2/DPPH\bullet}$ was common for all solvents and phenols. It will be briefly described for DOPPH• and **1** in hexane, but lower concentrations of the other phenols (and consequently lower concentrations of DOPPH•) were used in this solvent, because of their lower solubility. Solutions of DOPPH• (ca. 0.1 mM) and of **1** (five or six different concentrations in a range from 0.7 to 6.0 mM) were

prepared in hexane at ambient temperature. After filling the two syringes (2 mL each) of the stopped-flow apparatus, one with the DOPPH• solution and the other with the phenol solution, a slow flow of Ar or N_2 was bubbled for about 5 min through these solutions. The two solutions were then rapidly mixed in a 1:1 v/v ratio and passed into the measurement cell. The decay of the DOPPH• absorption was monitored at 519 nm. The decay traces were subsequently analyzed as pseudo-first-order processes to yield k^S_{exptl}. Plots of k^S_{exptl}/s^{-1} vs [**1**] were linear, and their slope gave the desired second-order rate constant, $k^S_{Ar(OH)_2/DPPH•}$.

Infrared Determination of K^i. Equilibrium constants, K^i, for formation of 1:1 complexes between phenols **1**−**6** and DMSO in CCl_4 at ambient temperature were determined as follows. Five or six solutions of the phenol in CCl_4 (concentration range 0.4−6 mM for the less soluble compounds and 1−10 mM for the more soluble) were used to generate a calibration curve for the absorbance of the "free" OH peak at about 3600 cm^{-1}. Excellent straight lines were obtained in all cases ($R^2 = 0.98-0.99$), showing that there was no self-association over the concentration of ranges employed. The spectra from five solutions containing the same concentration of phenol (usually a concentration in the middle of the calibration curve) and increasing concentrations of DMSO (range 0.7−6 mM) were recorded. The absorbance of the peak at ca. 3600 cm^{-1} gave, via the calibration curve, the concentration of free, i.e., non-DMSO H-bonded, phenol in solution, $[ArOH]_{free}$. At low concentrations of DMSO it is safe to assume that only 1:1 complexes will be formed. Therefore, $[ArOH]_{free}$ yields the equilibrium constant via the following simple equation (see Scheme 2):

$$[ArOH]_0/[ArOH]_{free} = 1 + K^i[DMSO]_{free}$$

where $[ArOH]_0$ is the analytical concentration of the phenol and $[DMSO]_{free}$ is the concentration of non-hydrogen-bonded DMSO in solution, which is equal to $[DMSO]_0 - ([ArOH]_0 - [ArOH]_{free})$. Plots of the ratio $[ArOH]_0/[ArOH]_{free}$ vs $[DMSO]_{free}$ were linear ($R^2 = 0.96-0.99$) at $[DMSO]_0 \leq 6$ mM, and their slope gave K^i.

HBA Additive-Induced Shift in the Frequency of the Intramolecularly H-Bonded OH Group of 1 in CCl_4. Increasing quantities of the HBA additive (usual range 3−100 mM) were added to a solution of ca. 3 mM **1** in CCl_4 until the pair of bands at 3617.7 and 3555.8 cm^{-1} disappeared and a new band at a frequency somewhat lower than 3555.8 cm^{-1} was clearly defined.

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Supporting Information Available: A full kinetic analysis of Scheme 2; IR-based data used to determine detailed kinetics results and plots of k_{exptl} vs $[Ar(OH)_2]$, from which the data in Table 1 were obtained; K^i for **1**−**5** + DMSO in CCl_4. This material is available free of charge via the Internet at http://pubs.acs.org.

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