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Kinetic Solvent Effects on Proton and Hydrogen Atom Transfers from Phenols. Similarities and Differences

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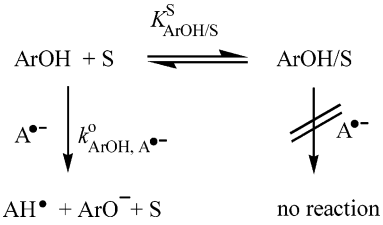
Abstract: Bimolecular rate constants for proton transfer from six phenols to the anthracene radical anion have been determined in up to eight solvents using electrochemical techniques. Effects of hydrogen bonding on measured rate constants were explored over as wide a range of phenolic hydrogen-bond donor (HBD) and solvent hydrogen-bond acceptor (HBA) activities as practical. The phenols' α_2^H values ranged from 0.261 (2-MeO-phenol) to 0.728 (3,5-Cl_2-phenol), and the solvents' β_2^H values from 0.44 (MeCN) to 1.00 (HMPA), where α_2^H and β_2^H are Abraham's parameters describing relative HBD and HBA activities (*J. Chem. Soc., Perkin Trans. 2* **1989**, 699; **1990**, 521). Rate constants for H-atom transfer (HAT) in HBA solvents, k^S, are extremely well correlated via $\log k^S = \log k^0 - 8.3\,\alpha_2^H\,\beta_2^H$, where k^0 is the rate constant in a non-HBA solvent (Snelgrove et al. *J. Am. Chem. Soc.* **2001**, *123*, 469). The same equation describes the general features of proton transfers (k^S decreases as β_2^H increases, slopes of plots of $\log k^S$ against β_2^H increase as α_2^H increases). However, in some solvents, k^S values deviate systematically from the least-squares $\log k^S$ versus β_2^H correlation line (e.g., in THF and MeCN, k^S is always smaller and larger, respectively, than "expected"). These deviations are attributed to variations in the solvents' anion solvating abilities (THF and MeCN are poor and good anion solvators, respectively). Values of $\log k^S$ for proton transfer, but not for HAT, give better correlations with Taft et al.'s (*J. Org. Chem.* **1983**, *48*, 2877) β scale of solvent HBA activities than with β_2^H. The β scale, therefore, does not solely reflect solvents' HBA activities but also contains contributions from anion solvation.

The kinetics for protonation of the anthracene radical anion ($A^{\bullet-}$) by phenol and 13 different methyl-substituted phenols (ArOH) in four solvents (S), dimethyl sulfoxide (DMSO), *N*,*N*-dimethylformamide (DMF), propylene carbonate (PC), and acetonitrile (MeCN) were reported by one of us some 13 years ago.[1] The observed rate constants were corrected for the stoichiometric effects of formation of the homoconjugation complexes, $ArOH/ArO^-$ and $ArOH/ArOH/ArO^-$, where "/" symbolizes a hydrogen bond between two species, and the kinetic contributions from protonation of $A^{\bullet-}$ by ArOH dimers to obtain the bimolecular rate constants, $k^S_{ArOH,A^{\bullet-}}$, in solvent S.

$$(ArOH)^S + (A^{\bullet-})^S \xrightarrow{k^S_{ArOH,A^{\bullet-}}} (ArO^-)^S + (AH^{\bullet})^S \qquad (1)$$

In these solvents, ArOH exists predominantly as the ArOH/S hydrogen-bond complex, with only minor amounts of "free" ArOH being present. It was proposed[1] that the protonation of $A^{\bullet-}$ involved *only* the free ArOH. Assuming that each proton donor molecule, ArOH, can act as a hydrogen-bond donor (HBD) only to a single hydrogen-bond acceptor (HBA) solvent molecule, S, at any one time, the kinetic situation can be illustrated by Scheme 1.

Scheme 1



Thus, there is a unique, solvent-independent rate constant for proton transfer, $k^0_{ArOH,A^{\bullet-}}$, which is given by

$$k^0_{ArOH,A^{\bullet-}} = k^S_{ArOH,A^{\bullet-}}\,(1 + K^S_{ArOH/S}\,[S]) \qquad (2)$$

This unique rate constant can be calculated from eq 2 with the assumption that the equilibrium constant, $K^S_{ArOH/S}$, is essentially independent of the medium.[1,2] That is, $K^S_{ArOH/S}$ can be equated to the readily measured (generally by IR spectroscopy) equilibrium constant for hydrogen bonding between ArOH and S as dilute solutes in tetrachloromethane as solvent:[2]

$$(ArOH)^{CCl_4} + (S)^{CCl_4} \rightleftharpoons (ArOH/S)^{CCl_4} \qquad (3)$$

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(1) Nielsen, M. F.; Hammerich, O. *Acta Chem. Scand.* **1992**, *46*, 883−896.
(2) Nielsen, M. F. *Acta Chem. Scand.* **1992**, *46*, 533−548.

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$$K^{S}_{ArOH/S} = K^{CCl_4}_{ArOH/S} \quad (4)$$

Three years later, these concepts, which had been developed for proton transfers from phenols, were found to be applicable to hydrogen atom abstractions from phenols (and other substrates) by the cumyloxyl free radical, eq 5 ($Y^{\bullet} = PhCMe_2O^{\bullet}$):[3]

$$(ArOH)^S + (Y^{\bullet})^S \xrightarrow{k^S_{ArOH,Y^{\bullet}}} (ArO^{\bullet})^S + (YH)^S \quad (5)$$

Moreover, it was recognized that the magnitude of the kinetic solvent effect (KSE) on reaction 5 (e.g., $k^{CCl_4}_{ArOH,Y\bullet}/k^{t-BuOH}_{ArOH,Y\bullet}$) would generally be independent of $Y^{\bullet}$ because the KSE is determined by the strength of the interaction between ArOH and the HBA solvent.[3] This was quickly confirmed,[4] and linear relationships were demonstrated[3−5] when the logarithm of the reaction rate constants in solvent S were plotted against Abraham et al's[6] empirical solute parameter, β^H_2, that is, linear free energy relationships were obtained in the form

$$\log(k^S_{ArOH,Y\bullet}/M^{-1}\,s^{-1}) = \log(k^0_{ArOH,Y\bullet}/M^{-1}\,s^{-1}) + M_{ArOH}\beta^H_2 \quad (6)$$

In this equation, (i) β^H_2 represents a general, thermodynamically related scale of solute hydrogen-bond acceptor abilities in CCl_4, values of β^H_2 range in magnitude from 0.00 for a non-HBA solvent, such as an alkane, to 1.00 for hexamethylphosphortriamide (HMPA), the strongest organic HBA; (ii) M_{ArOH} represents the magnitude of the KSE for the particular ArOH and any $Y^{\bullet}$ and is the slope of the straight line obtained by plotting $\log(k^S_{ArOH,Y\bullet})$ against β^H_2; and (iii) $\log(k^0_{ArOH,Y\bullet})$ is the intercept in this plot for $\beta^H_2 = 0.00$, which is also equal to the logarithm of the measured rate constants in an alkane solvent and corresponds to the unique rate constants for the reactants, ArOH and $Y^{\bullet}$.

The magnitude of M_{ArOH} clearly depended on the intrinsic ability of ArOH to form a linear, intermolecular hydrogen bond to an HBA molecule. Extensive kinetic measurements[7] involving hydrogen atom abstractions at ambient temperatures from a dozen substrates (mainly phenols) by *tert*-alkoxyl radicals and by 2,2-diphenyl-1-picrylhydrazyl radicals in up to a dozen solvents varying in β^H_2 from 0.00 to 0.49 demonstrated that M_{ArOH} values were proportional to the hydrogen-bond donating (HBD) abilities of ArOH, as scaled with Abraham et al's[8] α^H_2 parameters. These parameters represent a general, thermodynamically related scale of solute hydrogen-bond donating abilities in CCl_4 and range in magnitude from 0.00 (e.g., alkanes) to nearly 1.0 for strong acids (e.g., 0.951 for CF_3COOH). The α^H_2 values of the hydrogen-atom donor substrates which were studied[7] varied from 0.00 (cyclohexane[9] and 1,4-cyclohexadiene[10]) to 0.73 (3,5-dichlorophenol) and, for phenols only, from 0.26 (2-methoxyphenol) to 0.73. These data yielded the general, empirical equation[7]

$$\log(k^S_{ArOH,Y\bullet}/M^{-1}\,s^{-1}) = \log(k^0_{ArOH,Y\bullet}/M^{-1}\,s^{-1}) - 8.3\,\alpha^H_2\,\beta^H_2 \quad (7)$$

which describes and predicts KSEs for hydrogen-atom donors at ambient temperatures. Equation 7 is fairly reliable; its predictions always agreeing with experiments to within a factor of 3−5 and generally agreeing to better than a factor of 2. This is quite remarkable considering the range of substrate HBD activities ($\alpha^H_2 = 0.00-0.73$) and solvent HBA activities ($\beta^H_2 = 0.00-0.49$) examined. It serves to emphasize the dominant role of hydrogen bonding in determining the magnitudes of KSEs for hydrogen-atom abstraction reactions.

KSE data, which could be used to determine whether an equation essentially identical to eq 7 applies to proton transfers, appear to be limited to the reactions of phenols with the anthracene radical anion referred to above. That is, eq 8 appears eminently reasonable.

$$\log(k^S_{ArOH,A^{\bullet-}}/M^{-1}\,s^{-1}) = \log(k^0_{ArOH,A^{\bullet-}}/M^{-1}\,s^{-1}) - 8.3\,\alpha^H_2\,\beta^H_2 \quad (8)$$

Unfortunately, the available data[1] are too sparse to be definitive regarding the applicability of eq 8, though the rate constants measured for phenol ($\alpha^H_2 = 0.59$) and 2,4,6-trimethylphenol ($\alpha^H_2 = 0.37$) in the four solvents ($\beta^H_2 = 0.44-0.77$) are not inconsistent with this equation.[11]

The present work was therefore undertaken to investigate further the applicability of eq 8 to proton-transfer reactions, using six phenols with α^H_2 values ranging from 0.26 to 0.73 in (whenever possible) eight solvents having β^H_2 values ranging from 0.44 to 1.00. The rates of proton transfer were measured by derivative cyclic voltammetry (DCV) and/or linear sweep voltammetry (LSV). The measured rate constants were corrected for stoichiometric effects due to the formation of homoconjugation complexes and kinetic effects due to participation of phenol dimers as proton donors (see above).

Results

The solvents used in this study—*N*,*N*,*N*,*N*,*N*,*N*-hexamethylphosphortriamide (HMPA), triethyl phosphate (TEP), dimethyl sulfoxide (DMSO), *N*,*N*-dimethylformamide (DMF), tetrahydrofuran (THF), acetone, propylenecarbonate (PC), and acetonitrile (MeCN)—were chosen in order to obtain the widest possible range in hydrogen-bond acceptor strengths and a broad variety in functionality. Very weak hydrogen-bond accepting solvents, such as alkanes, could not be included since these are nonpolar and the electrochemical approach requires the solvent to have some polarity in order to dissolve the supporting electrolyte (in this case tetra-*n*-butylammonium hexafluorophosphate, Bu_4NPF_6) in order to obtain a conducting medium. Also, the use of media with low polarity would lead to strong ion pairing between the electrogenerated base, the anthracene radical anion, and the supporting electrolyte cations. Ion pairing would strongly influence the actual basicity of the radical anion

(3) Avila, D. V.; Ingold, K. U.; Lusztyk, J.; Green, W. H.; Procopio, D. R. *J. Am. Chem. Soc.* **1995**, *117*, 2929−2930.
(4) Valgimigli, L.; Banks, J. T.; Ingold, K. U.; Lusztyk, J. *J. Am. Chem. Soc.* **1995**, *117*, 9966−9971.
(5) MacFaul, P. A.; Ingold, K. U.; Lusztyk, J. *J. Org. Chem.* **1996**, *61*, 1316−1321.
(6) Abraham, M. H.; Grellier, P. L.; Prior, D. V.; Morris, J. J.; Taylor, P. J. *J. Chem. Soc., Perkin Trans. 2* **1990**, 521−529.
(7) Snelgrove, D. W.; Lusztyk, J.; Banks, J. T.; Mulder, P.; Ingold, K. U. *J. Am. Chem. Soc.* **2001**, *123*, 469−477.
(8) Abraham, M. H.; Grellier, P. L.; Prior, D. V.; Duce, P. P.; Morris, J. J.; Taylor, P. J. *J. Chem. Soc., Perkin Trans. 2* **1989**, 699−711.
(9) Avila, D. V.; Brown, C. E.; Ingold, K. U.; Lusztyk, J. *J. Am. Chem. Soc.* **1993**, *115*, 466−470.
(10) Wayner, D. D. M.; Lusztyk, E.; Pagé, D.; Ingold, K. U.; Mulder, P.; Laarhoven, L. J. J.; Aldrich, H. S. *J. Am. Chem. Soc.* **1995**, *117*, 8737−8744.
(11) See Figure 5 in ref 7.

Table 1. Selected Parameters Characterizing the Eight Solvents Used in This Work

solvent[a]	β_2^{H}[b,c]	β[b,d]	$\Sigma\beta_2^{H}$[b,e]	ϵ_r[f]	π^*[g]	η/mPa·s[f]	E_T^N[h]	A[i]
HMPA	1.00[j]	1.05	1.60	29.30	0.87	3.11	0.315	0.00[j]
DMSO	0.78	0.76	0.88	46.45	1.00	1.991	0.444	0.34
TEP	0.77[k]	0.77	1.06	10.79	0.72	2.147	0.324	
DMF	0.66	0.69	0.74	36.71	0.88	0.802	0.386	0.30
THF	0.51	0.55	0.48	7.58	0.58	0.462	0.207	0.17
acetone	0.50	0.48	0.49	20.56	0.71	0.303	0.355	0.25
PC	0.50	0.40		64.92	0.83	2.53	0.472	
MeCN	0.44	0.31	0.32	35.94	0.75	0.341	0.460	0.37

[a] The abbreviations are defined in the text. [b] Hydrogen-bond acceptor strength as described in the text. [c] Values are from ref 6 except for the value for PC, which is from ref 14. [d] From ref 15. [e] From ref 16. [f] Relative permittivity, ϵ_r, and viscosity, η, both at 25 °C are from the compilations in ref 17. [g] Dielectric solvation parameter, π^*, from ref 15. [h] Normalized $E_T(30)$ solvent polarity parameters from ref 13. [i] Acity, ref 18. [j] Arbitrary anchor point. [k] Value for the generic $(RO)_3PO$.

and, thereby, the kinetics of the proton-transfer reaction. Another criterion which has to be fulfilled by the chosen solvents is that they should be more difficult to reduce electrochemically than anthracene (≈ -2 V vs SCE) and not be prone to reduction electrocatalytically, that is, by electron transfer from the anthracene radical anion. This excludes several halogenated solvents. Only non-HBD solvents[12] can be employed. Finally, anthracene should be soluble in millimolar amounts in the chosen solvents. Values for those solvent parameters discussed in this study are given in Table 1 for the eight solvents mentioned above.

The six phenols used as proton donors were 2-methoxyphenol, 2,4,6-trimethylphenol, 4-methoxyphenol, phenol, 4-(trifluoromethyl)phenol, and 3,5-dichlorophenol. They were chosen from among those used in the study of KSEs on hydrogen-atom abstraction[7] and greatly extend the range of thermodynamic acidities and hydrogen-bond donor strengths with respect to the previous study of KSEs on proton transfer from phenols.[1] The 2-methoxyphenol is of specific interest because the formation of a *nonlinear* (bent) intramolecular hydrogen bond does not prevent a fast H-atom abstraction by *tert*-alkoxyl radicals.[7,19] However, it does greatly reduce the ability of this phenol to act as an HBD because formation of an intermolecular H-bond does not break the intramolecular H-bond but leads to a bifurcated H-bond.[19] The six phenols and their relative HBD abilities, as given by Abraham et al.'s α_2^H values,[8] are listed in Table 2. This table also includes their measured pK_a in water[20] and thermodynamic acidities in DMSO[21] and differences in their homolytic O−H bond dissociation enthalpies, ΔBDE [=BDE(ArO−H) − BDE(PhO−H)].[22]

Table 2. Selected Parameters Characterizing the Six Phenols Used in This Work

phenol	α_2^H[a]	pK_a[b]	pK_{DMSO}[c]	ΔBDE (kcal/mol)[d]
3,5-$Cl_2C_6H_3OH$	0.728	8.19	13.56	5.3
4-$CF_3C_6H_4OH$	0.680	8.68	15.2	4.1
C_6H_5OH	0.590	9.99	18.0	(0)
4-$MeOC_6H_4OH$	0.550	10.21	19.1	−5.2
2,4,6-$Me_3C_6H_2OH$	0.374[e]	10.86	19.6[f]	−4.8
2-$MeOC_6H_4OH$	0.261[e]	9.98	17.8	−3.2

[a] From ref 7 unless otherwise noted. [b] From ref 20. [c] From ref 21. [d] Calculated from an equation given in ref 22. Rather similar values can be calculated from equations given in refs 23 and 24. For reliable experimental data pertaining to the effect of ring substituents on the O−H BDEs of these and related phenols, see ref 25. [e] From ref 8. [f] Estimated from relationships given in ref 2.

Table 3. Second-Order Rate Constants (21 ± 1 °C unless otherwise noted) for Proton Transfer to the Anthracene Radical Anion, 10^{-4} $k^S_{ArOH,A^{\bullet-}}/M^{-1}$ s^{-1}, from the Six Phenols in the Eight Solvents Corrected for Stoichiometric Effects of Homoconjugation, Kinetic Contributions from Phenol Dimers, and (for the fastest reactions) from the Effects of the Rate of the Heterogenous Electron Transfer and Contributions from the ECE Mechanism (see Experimental Section and Supporting Information for details; rate constants in parentheses are from ref 1)

	Phenol Substituents					
solvent	2-MeO	2,4,6-Me_3	4-MeO	none	4-CF_3	3,5-Cl_2
HMPA					1.0	2.7
DMSO	0.24	0.057 (0.066)[a]	0.081	0.29 (0.34)[a]	12	73
TEP	0.31	0.091	0.051	0.27	27	150
DMF	0.38	0.13 (0.15)[a]	0.16	0.50 (0.58)[a]	53	270
THF	0.43	0.23	0.19	1.0	85	760
acetone	1.5	0.62	0.95	2.6	410	2600
PC	6.4[a]	1.1[a] (0.59)[a]	6.1[a]	13 (13)[a]	670	2000
MeCN	9.3	1.9 (1.7)[a]	8.8	27 (28)[a]	1500	8500

[a] At 25 ± 1 °C.

Second-order rate constants, $k^S_{ArOH,A^{\bullet-}}$, for protonation of the anthracene radical anion by the six phenols in the various solvents are presented in Table 3. Details of the determination of these rate constants by electrochemical measurements, the experimental procedures employed, and details regarding the various corrections required are given in the Experimental Section with additional details in the Supporting Information.

The rate constants obtained in the present work, generally at 21 °C, for phenol and 2,4,6-Me_3-phenol, each in four solvents (DMSO, DMF, PC, and MeCN), can be compared with the 25 °C rate constants reported originally.[1] These "old" rate constants are included (in parentheses) in Table 3. With the single exception of 2,4,6-Me_3-phenol in PC, the agreement between the two data sets is outstanding. This lends confidence to our belief that the numbers in Table 3 do, indeed, represent the second-order rate constants for proton transfer to the anthracene radical anion from the phenols in the different solvents, 10^{-4} $k^S_{ArOH,A^{\bullet-}}/M^{-1}$ s^{-1}.

Discussion

"*When investigating solution-phase reaction kinetics, the problems to be faced include deciding which property of the solvent to use when setting up mathematical correlations with the reaction rates. Another problem is deciding which charac-*

(12) Reichardt[13] recommends "non-HBD" solvent as a replacement for "aprotic" and "dipolar aprotic" solvent because solvents such as DMSO and MeCN can reveal protic character in reactions with strong bases; see ref 13, Chapter 2, p 18.
(13) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 3rd ed.; Wiley-VCH: Weinheim, Germany, 2003.
(14) Besseau, F.; Laurence, C.; Berthelot, M. *J. Chem. Soc., Perkin Trans. 2* **1994**, 485−489.
(15) Kamlet, M. J.; Abboud, J.-L. M.; Abraham, M. H.; Taft, R. W. *J. Org. Chem.* **1983**, *48*, 2877−2887.
(16) (a) Abraham, M. H. *Chem. Soc. Rev.* **1993**, 73−83. (b) Abraham, M. H. *NATO ASI Series C* **1994**, *426*, 63−78. (c) Abraham, M. H.; Andonian-Haftvan, J.; Whiting, G. S.; Leo, A.; Taft, R. W. *J. Chem. Soc., Perkin Trans. 2* **1994**, 1777−1791.
(17) Marcus, Y. *The Properties of Solvents*; Wiley: Chichester, England, 1998.
(18) Swain, C. G.; Swain, M. S.; Powell, A. L.; Alunni, S. *J. Am. Chem. Soc.* **1983**, *105*, 502−513.
(19) de Heer, M. I.; Mulder, P.; Korth, H. G.; Ingold, K. U.; Lusztyk, J. *J. Am. Chem. Soc.* **2000**, *122*, 2355−2360.
(20) Serjeant, E. P.; Dempsey, B. *Ionization Constants of Organic Acids in Aqueous Solution*; IUPAC Chemical Data Series-No. 23; Pergamon: Oxford, England, 1979.
(21) Bordwell, F. G.; Cheng, J.-P. *J. Am. Chem. Soc.* **1991**, *113*, 1736−1743.
(22) Pratt, D. A.; de Heer, M. I.; Mulder, P.; Ingold, K. U. *J. Am. Chem. Soc.* **2001**, *123*, 5518−5526.

teristics of the reacting molecules are to be considered when the effects of the solvent on their reactivity is determined."[13]

In seven solvents, S, the second-order rate constant for proton transfer to the anthracene radical anion, $k^{S}_{ArOH,A^{\bullet-}}$, could be measured for all six phenols (Table 3). In these solvents, the most reactive compound was always 3,5-$Cl_2C_6H_3OH$, while 2,4,6-$Me_3C_6H_2OH$ was the least reactive in five of the solvents and 4-$MeOC_6H_4OH$ was least reactive in two solvents, TEP and THF. In each solvent, the ratio of $k^{S}_{ArOH,A^{\bullet-}}$ for the most reactive phenol to $k^{S}_{ArOH,A^{\bullet-}}$ for the least reactive phenol was a bit greater than 3 orders of magnitude (range in ratios ~1300 in DMSO to ~4500 in MeCN). With three minor exceptions, which may well be due to experimental errors, the values of $k^{S}_{ArOH,A^{\bullet-}}$ for the six phenols increase along the solvent series: HMPA < DMSO < TEP < DMF < THF < acetone < PC < MeCN, with k^{MeCN}/k^{DMSO} ratios ranging from a low of 33 for 2,4,6-$Me_3C_6H_2OH$ to a high of 125 for 4-$CF_3C_6H_4OH$. The three slightly anomalous phenol/solvent pairs are 4-$MeOC_6H_4OH$/TEP: DMSO, C_6H_5OH/TEP: DMSO, and 3,5-$Cl_2C_6H_3OH$/PC: acetone, where *k* in the "expected" faster solvent (TEP or PC) has only 63, 93, and 77%, respectively, of its magnitude in the "expected" slower solvent (DMSO or acetone).

In any analysis of solvent effects on chemical reactions, it is customary to seek a linear relationship between some empirical solvent parameters and the logarithm of the rate constant for reaction, that is, a linear-free energy relationship.[13] There are a large number of parameters which purport to measure the relative HBA abilities of different solvents,[13] but it seems probable that many of these empirical parameters are "contaminated" by contributions from other types of solvent effects, such as dipolarity, polarizability, etc.[26] The most reliable scales of relative HBA activities of common organic solvents would appear to be the 1983 β-constants of Taft and co-workers[15,27] and various "sons of β" which have mainly been fathered by Abraham and co-workers in subsequent years.[28] The different β scales of solvent or solute hydrogen-bond basicity were generally derived (often along with other parameters which measure other solvent properties) by averaging multiple normalized solvent effects on a variety of properties involving many different types of indicators. Fortunately, the various β values for a specific HBA are frequently quite similar and often even identical. This is illustrated by the β_2^H and β values for HMPA, DMSO, TEP, DMF, THF, and acetone given in Table 1, the β_2^H and β values differ by $\geq$0.10 only for PC and MeCN (vide infra). However, the $\sum\beta_2^H$ values, which are supposed to be applicable when a solute is surrounded by solvent molecules[16,33] and which, therefore, would be expected to be close to β values, are very different from the β values for the three strongest HBAs: HMPA, DMSO, and TEP (Table 1).

The increase in $k^{S}_{ArOH,A^{\bullet-}}$ for the six phenols along the solvent series, HMPA < DMSO < TEP < DMF < THF < acetone < PC < MeCN (see Table 3), clearly parallels the decreasing HBA activities of these solvents as quantified by their β_2^H [6,14] and β [15,27] values (but not $\sum\beta_2^H$, see DMSO vs TEP); see Table 1. These KSEs do not parallel the ϵ_r, π^*, η, E_T^N, or *A* values for these solvents (also given in Table 1). Therefore, hydrogen bonding from the HBD phenols to the HBA solvents (Scheme 1) is *primarily* responsible for the KSEs for proton transfer from the phenols to the anthracene radical anion (reaction 1), as originally hypothesized from more limited data.[1,2]

In initial studies on KSEs for H-atom abstraction from phenol by a *tert*-alkoxyl radical,[3−5] we chose[5] to correlate our kinetic data with β_2^H despite the fact that this is a scale of solute hydrogen-bond basicities in CCl_4,[6,30] rather than a scale for neat solvents. This choice was made for four pragmatic reasons. First, the β_2^H scale is the most extensive of all β scales with values tabulated for at least 400 organic compounds.[16c] Second, the β_2^H value for a "new" HBA can be readily determined by IR spectroscopy using a few "calibrated" HBDs.[6] In contrast, the β values of Taft and co-workers[15] were obtained by averaging solvent effects on a variety of systems, and only after a series of successive approximations did most β values "settle down" and become "reliable". Third, among the dozen or so solvents employed,[3−5] there was one, *tert*-butyl alcohol, for which only a "nonreliable" β value (1.01 vs a reliable $\beta_2^H = 0.49$) appeared to be available and one, acetic acid, for which there appeared to be neither a β nor a β_2^H value, though there was a β_2^H for butyric acid (0.42).[35] Finally, and of overriding importance, the log $k^{S}_{PhOH,t-RO\bullet}/M^{-1}\ s^{-1}$ data gave a good linear free-energy relationship when plotted against β_2^H (S), including the points for the solvents (β_2^H): acetic acid (assumed 0.42), acetonitrile (0.44), and *tert*-butyl alcohol (0.49); see Figure 1 in ref 5. The plots against β using values of 0.31 for acetonitrile and ca. 1.0 for *tert*-butyl alcohol gave very poor linear correlations. Plots of log $k^{S}_{ArOH,t-RO\bullet}$ for a number of ring-substituted phenols also gave much better linear correlations with β_2^H than with β,[7,37] and we have continued to correlate KSEs for *hydrogen-atom* abstraction reactions with β_2^H.[39]

(23) Jonsson, M.; Lind, J.; Eriksen, T. E.; Merényi, G. *J. Chem. Soc., Perkin Trans. 2* **1993**, 1567−1568.
(24) Wayner, D. D. M.; Lusztyk, E.; Ingold, K. U.; Mulder, P. *J. Org. Chem.* **1996**, *61*, 6430−6433.
(25) (a) Mulder, P.; Saastad, O. W.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 4090−4092. (b) Lucarini, M.; Pedrielli, P.; Pedulli, G. F.; Cabiddu, S.; Fattuoni, C. *J. Org. Chem.* **1996**, *61*, 9259−9263. (c) de Heer, M. I.; Korth, H.-G.; Mulder, P. *J. Org. Chem.* **1999**, *64*, 6969−6975. (d) Brigati, G.; Lucarini, M.; Mugnaini, V.; Pedulli, G. F. *J. Org. Chem.* **2002**, *67*, 4828−4832.
(26) For example, this would appear to be the case for Swain et al.'s[18] solvent "basity" parameter, *B*. For an interesting discussion of this point, see: (a) Taft, R. W.; Abboud, J.-L. M.; Kamlet, M. J. *J. Org. Chem.* **1984**, *49*, 2001−2005. (b) Swain, C. G. *J. Org. Chem.* **1984**, *49*, 2005−2010.
(27) See also: Marcus, Y.; Kamlet, M. J.; Taft, R. W. *J. Phys. Chem.* **1988**, *92*, 3613−3622.
(28) There would appear to be at least seven "sons of β": β_m, for monomeric (nonself-associated) material;[29] β_2^H, a general, thermodynamically related, scale of solute hydrogen-bond basicities in CCl_4;[6,30] β_1(general), β_1(special), two scales of solvent hydrogen-bond basicity;[31] β_2 (pK_{HB}), a special solute scale for hydrogen-bond complexation of bases with 4-fluorophenol in CCl_4;[31] β_{sm}, a basicity scale based on extrapolation to infinite dilution;[32] and $\sum\beta_2^H$, a scale of effective or summation hydrogen-bond basicity appropriate for situations in which a solute is surrounded by solvent molecules.[16,33,34]
(29) Taft, R. W.; Abboud, J.-L. M.; Kamlet, M. J.; Abraham, M. H. *J. Solution Chem.* **1985**, *14*, 153−175.
(30) See also: (a) Abraham, M. H.; Grellier, P. L.; Prior, D. V.; Taft, R. W.; Morris, J. J.; Taylor, P. J.; Laurence, C.; Berthelot, M.; Doherty, R. M.; Kamlet, M. J.; Abboud, J.-L. M.; Sraidi, K.; Guihéneuf, G. *J. Am. Chem. Soc.* **1988**, *110*, 8534−8536. (b) Abraham, M. H.; Grellier, P. L.; Prior, D. V.; Morris, J. J.; Taylor, P. J. *Tetrahedron Lett.* **1989**, *30*, 2571−2574. (c) Laurence, C.; Berthelot, M.; Helbert, M.; Sraidi, K. *J. Phys. Chem.* **1989**, *93*, 3799−3802. (d) Abraham, M. H.; Lieb, W. R.; Franks, N. P. *J. Pharm. Sci.* **1991**, *80*, 719−724.
(31) Abraham, M. H. et al. *J. Phys. Org. Chem.* **1989**, *2*, 540−552.
(32) Abraham, M. H.; Duce, P. P.; Prior, D. V.; Barratt, D. G.; Morris, J. J.; Taylor, P. J. *J. Chem. Soc., Perkin Trans. 2* **1989**, 1355−1375.
(33) Abraham, M. H. *J. Phys. Org. Chem.* **1993**, *6*, 660−684.
(34) For reviews of various β scales, see: Abraham, M. W. *Port. Electrochim. Acta* **1992**, *10*, 121−134, and ref 16.
(35) The current β values for *tert*-butyl alcohol and acetic acid are 0.93 and 0.45, respectively, but it is not clear whether these values are considered "reliable".[36]
(36) See ref 13, p 433, and ref 17, pp 146 and 148.

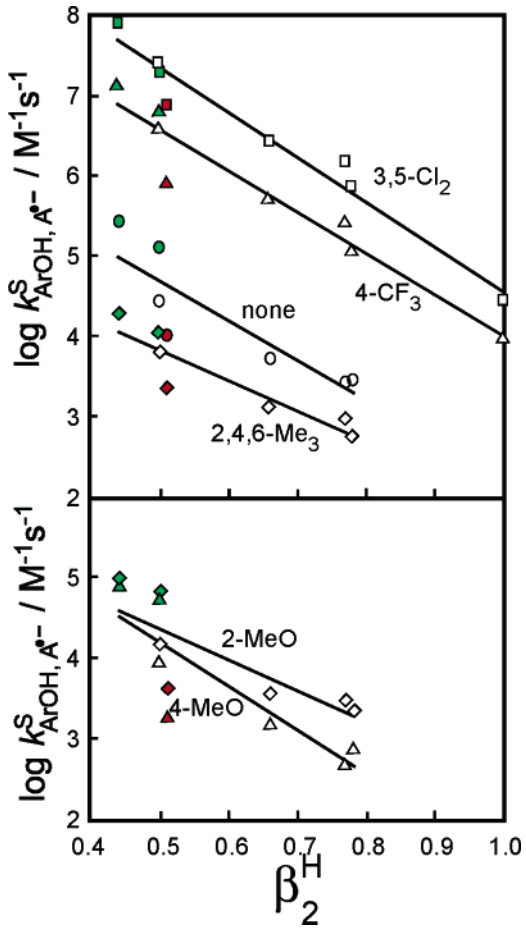


Figure 1. Plots of log $k^S_{ArOH,A^{\bullet-}}$ against β_2^H. Upper panel: □, 3,5-dichlorophenol; △, 4-(trifluoromethyl)phenol; ○, phenol; ◇, 2,4,6-trimethylphenol. Lower panel: ◇, 2-methoxyphenol; △, 4-methoxyphenol. The solvents and their β_2^H values are: MeCN, 0.44 (points shown in green); PC, 0.50 (points shown in green); acetone, 0.50; THF, 0.51 (points shown in red); DMF, 0.66; TEP, 0.77; DMSO, 0.78; HMPA, 1.00.

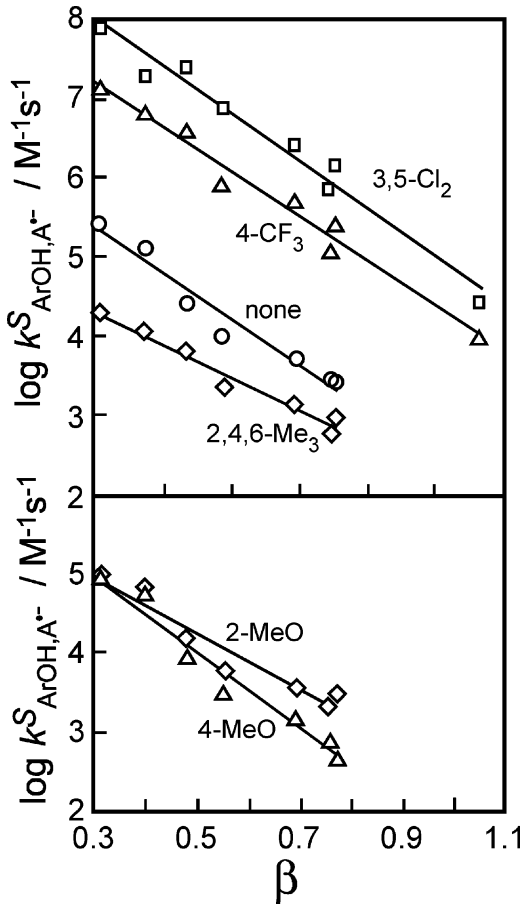


Figure 2. Plots of log $k^S_{ArOH,A^{\bullet-}}$ against β. Upper panel: □, 3,5-dichlorophenol; △, 4-(trifluoromethyl)phenol; ○, phenol; ◇, 2,4,6-trimethylphenol. Lower panel: ◇, 2-methoxyphenol; △, 4-methoxyphenol. The solvents and their β values are: MeCN, 0.31; PC, 0.40; acetone, 0.48; THF, 0.55; DMF, 0.69; DMSO, 0.76; TEP, 0.77; HMPA, 1.05.

With the foregoing in mind, we have plotted the present *proton* transfer kinetic data for all six phenols against β_2^H (Figure 1) and against β (Figure 2), reliable values of β being available for all eight solvents.[15] Least-squares lines have been drawn through the experimental points (Table 3), and their slopes, R^2 values, and intercepts, which correspond to log k^0/M^{-1} s^{-1}, are summarized in Table 4. Plots of log $k^S_{ArOH,A^{\bullet-}}/M^{-1}$ s^{-1} against $\sum\beta_2^H$ are not shown because they exhibit considerably more scatter than the plots shown for the same phenol in Figures 1 and 2, this scatter arising from the large differences between $\sum\beta_2^H$ values and the β_2^H and β values for HMPA, DMSO, and TEP (see Table 1).

Even a simple visual inspection of Figures 1 and 2 reveals that the kinetic data for these proton transfers (reaction 1) give much better linear free-energy relationships when plotted against β than when plotted against β_2^H. This is confirmed by the R^2 values listed in Table 4. The main reasons for the better "fit" to β arise from the significant differences between the β and β_2^H values for the solvents MeCN, PC, and THF (see Table 1). The R^2 values for the β_2^H plots for the individual phenols decrease significantly as the phenols' α_2^H values (Table 2) decrease and as the rate constants for the different phenols in a particular solvent (Table 3) decrease. This trend is not apparent in the R^2 values for the plots against β (except, possibly, in the case of 2-methoxyphenol).

Table 4. Slopes Predicted by Equation 8 for Plots of log $k^S_{ArOH,A^{\bullet-}}/M^{-1}$ s^{-1} versus β_2^H and Experimental Least-Squares Slopes (R^2) and Intercepts Derived from Plots of log $k^S_{ArOH,A^{\bullet-}}/M^{-1}$ s^{-1} versus β_2^H (Figure 1) and versus β (Figure 2)

phenol substituents	predicted slope[a]	Experimental β_2^H Plot[b] slope	(R^2)	intercept[c]	Experimental β Plot[d] slope	(R^2)	intercept[c]
3,5-Cl_2	−6.04	−5.55	(0.96)	10.13	−4.52	(0.97)	9.38
4-CF_3	−5.64	−5.14	(0.92)	9.17	−4.28	(0.98)	8.53
None	−4.90	−4.94	(0.76)	7.16	−4.32	(0.95)	6.67
4-MeO	−4.57	−5.40	(0.71)	6.89	−4.78	(0.92)	6.39
2,4,6-Me_3	−3.10	−3.77	(0.84)	5.71	−3.15	(0.97)	5.25
2-MeO	−2.17	−3.74	(0.65)	6.23	−3.41	(0.89)	5.94

[a] Equation 8. [b] Figure 1. [c] log $k^0_{ArOH,A^{\bullet-}}/M^{-1}$ s^{-1}. [d] Figure 2.

The negative slopes of the β_2^H and β plots (Figures 1 and 2) *prove* that the KSEs for the proton-transfer reactions studied in the present work are *primarily* a consequence of the inactivation

(37) This includes α-tocopherol (vitamin E) if all the data points are included.[7] We have, however, noted[38] that *provided* the points for *tert*-butyl alcohol, acetic acid, and water are (arbitrarily) *excluded* then, *for this phenol only*, there is a better fit with β than with β_2^H(due solely to β being $\ll \beta_2^H$ for acetonitrile (see Table 1).

(38) Valgimigli, L.; Ingold, K. U.; Lusztyk, J. *J. Am. Chem. Soc.* **1996**, *118*, 3545−3549.
(39) (a) Litwinienko, G.; Ingold, K. U. *J. Org. Chem.* **2003**, *68*, 3433−3438. (b) Litwinienko, G.; Ingold, K. U. *J. Org. Chem.* **2004**, *69*, 5888−5896. (c) Foti, M.; Sortino, S.; Ingold, K. U. *Chem.—Eur. J.* **2005**, *11*, 1942−1948.

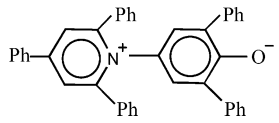
of a certain (large) fraction of the phenols by their hydrogen bonding to solvent molecules (Scheme 1), as was hypothesized originally.[1,2] The fact that KSEs for hydrogen-atom transfers from neutral phenols to neutral radicals correlate better with β_2^H,[7] whereas KSEs for proton transfer from neutral phenols to the anthracene radical anion correlate better with β is *clearly* a consequence of the migration of the negative charge from the highly delocalized anion, $A^{\bullet-}$, to a much more localized anion, ArO^- (eq 1). That is, in addition to the very obvious kinetic effects of hydrogen bonding in these proton transfers, there is a contribution to the kinetics from the abilities of the different solvents to solvate anions. As the R^2 values for the β_2^H plots (Table 4) clearly demonstrate, and as would be predicted by classical kinetics, the importance of these anion solvation effects are greater for the less reactive proton donors, which are, of course, also the weaker HBDs.

The contrast in the linear free-energy relationships for hydrogen-atom transfers (β_2^H correlations)[7] and the present proton-transfer reactions (β correlations) is, in our opinion, a strong indication that β is not a "clean" measure of HBA activity. Values of β_2^H are derived from the experimental equilibrium constants for the formation of 1:1 hydrogen-bonded complexes between dilute HBDs and dilute (calibrated) HBAs in CCl_4 at 25 °C.[6] The strengths of these 1:1 complexes would appear not to be significantly altered by changing the solvent from CCl_4 to the neat HBA.[2,5,7] It is, therefore, not surprising that KSEs for H-atom transfers in neat HBA solvents correlate rather well with β_2^H.[40] However, β values "were arrived at by averaging multiple normalized solvent effects on a variety of properties involving many diverse types of indicators",[15] and it is therefore reasonable to conclude that β values contain contributions from components relevant to the present proton-transfer reactions.

Various factors might produce solvent-dependent changes in the driving force for these reactions (and thus help to account for the differences between β_2^H and β). These factors include (i) changes in nonspecific electrostatic solvation energies of a charged species, (ii) changes in specific solvation energy of a charged species, and (iii) ion pairing between anionic reactants and the cations of the supporting electrolyte necessary for the electrochemical measurements.

While it seems unlikely that just one of the above-mentioned three possible factors is wholly responsible for the deviations observed in the plots of log $k^S_{ArOH,A^{\bullet-}}$ versus β_2^H (Figure 1), it is still worth considering which factor is the most important. Changes in nonspecific solvation energies should be reflected by differences in the relative permittivities (dielectric constants) of the pure solvents, ϵ_r[42] (see Table 1). At first glance, this looks promising because the unusually "slow" solvent, THF (in which the kinetic points for all phenols fall below the least-squares lines through the points for all solvents and *have been colored red* in Figure 1), has the lowest ϵ_r value (7.58). However, nonspecific solvation can be eliminated as the dominant factor because of the reaction rates in TEP and DMSO. These two solvents have essentially identical β_2^H values but very different ϵ_r values (10.79 for TEP and 46.45 for DMSO, see Table 1). Thus, TEP would be predicted to be a "slow" solvent with all its kinetic points falling below the least-squares lines, while DMSO would be predicted to be a "fast" solvent with all its kinetic points falling above these lines, if nonspecific solvation were important. These predictions are not borne out by experiment (see Figure 1).

Solvent-induced changes in specific solvation energies of charged species would presumably arise in the conversion of the delocalized anion, $A^{\bullet-}$, into a much more localized anion (vide supra). Differences in anion solvation energies between solvents will be smaller for the delocalized $A^{\bullet-}$ reactant than for the more localized ArO^- product. Therefore, solvents with high anion-stabilizing activities would be expected to stabilize ArO^- relative to $A^{\bullet-}$ more strongly than those with low anion stabilizing activities. The former should therefore enhance the rate of reaction 1 and be "fast" solvents, while the latter will depress the rate of reaction and be "slow" solvents. There are several empirical scales of solvents' anion solvating abilities.[18,43] The most appropriate for families of reactions yielding alkoxides, as well as the most comprehensive empirical solvent polarity scale, would appear to be Dimroth and Reichardt's[44] $E_T(30)$ values and their more modern, normalized E_T^N values[45,46] (see Table 1). The $E_T(30)$ values are based on the transition energies for the longest wavelength solvatochromic band of the pyridinium-*N*-phenolate betaine dye, PPB.



PPB

The negative charge in PPB is rather localized on the phenolic oxygen atom because of twisting of the pyridinium and phenolate rings (interplanar angle ~ 65°) and twisting of the adjacent phenyl groups.[46] However, the positive charge on the pyridinium moiety is delocalized.[46] Therefore, the $E_T^N[E_T(30)]$ values *predominantly* measure the specific HBD activities and Lewis acidities of organic solvents. $E_T^N[E_T(30)]$ values have also been shown[43] to correlate with Swain et al.'s[18] solvent acities, *A* (see Table 1), which reflect the relative anion-solvating abilities of solvents. We have chosen to discuss solvent deviations from the least-square lines of Figure 1 in terms of the E_T^N values of the solvents rather than the *A* values because the latter are available for only six out of our eight solvents.

By a wide margin, the smallest E_T^N value for any of the solvents used in the present work is that for THF, 0.207 (see Table 1), which is only 56% of the mean E_T^N value of 0.370 for the eight solvents employed. Therefore, THF has a much poorer anion-solvating activity than any of the other solvents. This is congruent with our hypothesis that poor anion solvators will be "slow" solvents since the rate constants in THF for all six phenols (shown in red in Figure 1) fall well below the least-

(40) The formalism of the KSE scheme for H-atom transfer (which is the same as that for proton transfer, Scheme 1) implies that in neat solvents β_2^H values should possibly be corrected to acknowledge the fact that concentrations of neat solvents, though similar, are not identical. In earlier work on H-atom transfers in families of ester and nitrile solvents, such corrections met with little or no success.[5] Since we prefer not to create yet another scale of solvent polarity,[41] this matter will not be touched on further.

(41) Around 35 different solvent scales are already known!; see ref 13, p 445.

(42) Or, alternatively, by differences in π^*, which is an index of solvent dipolarity/polarizability measuring the ability of a solvent to stabilize a charge (or dipole) by virtue of its dielectric effect.[15] However, the kinetic data in "slow" and "fast" solvents correlate no better with π^* than with ϵ_r.

(43) See ref 13, pp 462−465.

(44) Dimroth, K.; Reichardt, C. *Liebigs Ann. Chem.* **1969**, *727*, 93−105.

(45) Reichardt, C.; Harbusch-Görnert, E. *Liebigs Ann. Chem.* **1983**, 721−743.

(46) See ref 13, pp 416−428.

squares lines. The next smallest E_T^N is that for HMPA (0.315), which is the strongest HBA ($\beta_2^H = 1.00$) and in which proton-transfer rate constants were only fast enough to be measured for two phenols; see Experimental. Since HMPA is also (necessarily) an "end point" in the Figure 1 plots, it is not possible to determine whether it is a relatively slow solvent. The highest E_T^N values are those for PC (0.472, 128% of the mean) and acetonitrile (0.460, 124% of the mean). These are fast solvents with the rate constants in PC and MeCN (both colored green in Figure 1) generally being well above the least-squares lines. The rate "enhancements" due to anion solvation effects in PC and MeCN are more apparent (against the large background KSE arising from hydrogen-bonding effects) for the less reactive phenols.[47] These results are also consistent with our hypothesis that anion solvation, or lack thereof, would manifest itself most strongly with phenols of low reactivity *and* relatively poor HBD activities.

Since differential anion solvation activities (factor (ii) above) provides a reasonable, though only qualitative, explanation for the observed lower and higher rate constants in certain solvents than would be expected from the data in other solvents, it would be fruitless to consider the possible role of ion pairing (factor (iii) above) as a potential explanation for the deviations from the least-squares lines in Figure 1 and from eq 8 (see also predicted slopes in Table 4).

There are, in our opinion, insufficient proton-transfer kinetic data (Table 3) to justify any attempt at their quantitative fitting using a two parameter, $C_1\beta_2^H + C_2E_T^N$, approach despite its attractions (which arise because both of these parameters are firmly established or can be unequivocally obtained by simple spectroscopic measurements). Similarly, our kinetic data should not be used to construct yet another solvent parameter scale.[41] However, the good-to-excellent linear fits obtained by plotting log $k^S_{ArOH,A^{\bullet-}}$ against β (Figure 2) are not as gratifying as might, at first, be thought. First, the slopes of log k versus β_2^H are predicted by the empirical eq 8 (and for H-atom transfers by eq 7), and therefore, the deviation of each kinetic point from its predicted value is meaningful and requires an explanation. Our explanation for the "deviations" of the proton-transfer rate constants for reaction 1 relies on the differences in the anion-solvating activities of our eight solvents. However, what do the least squares slopes of the plots of log k versus β (Table 4) mean? Certainly they fit no obvious pattern relating to any of the phenols' properties. In addition, there are serious problems with the β scale. As already mentioned, it is based on averaged, multiple normalized solvent effects on various properties. Reichardt[48] has emphasized the practical reasons which favor experimentally derived parameters obtained from a distinct, single, and well-understood solvent-dependent reference process (such as those yielding β_2^H and E_T^N) over averaged and statistically optimized solvent parameters. This is because the latter are not directly related to a distinct reference process, are subject to change as new measurements are made and are, therefore, ill-defined.[49] In addition, it would appear that the β scale is mainly based on solvent HBA basicity against NH donor solutes and does not have the general validity originally claimed.[51] The better linear fits obtained by plotting log $k^S_{ArOH,A^{\bullet-}}$ against β (Figure 2) compared with plots against β_2^H (Figure 1) further confirms that the β scale does not solely reflect HBA activities and implies that it contains contributions from the anion-solvating abilities of solvents.[52]

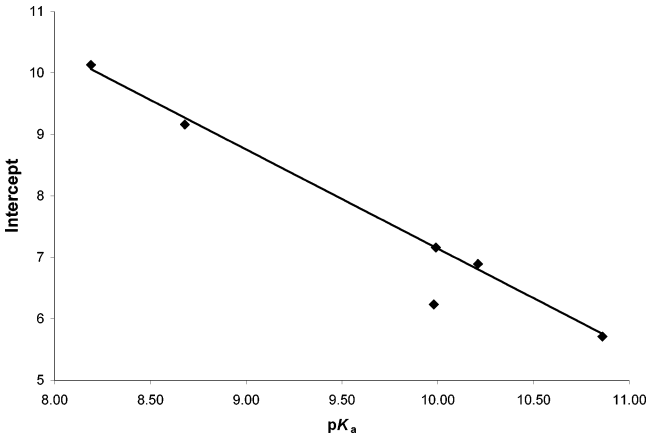


Figure 3. Intercepts at $\beta_2^H = 0$ from Figure 1 (see Table 4) plotted against pK_a. The outlier is the point for 2-methoxyphenol. The other five phenols yield the equation $\log(k^0_{ArOH,A^{\bullet-}}/M^{-1}\ s^{-1}) = 23.3 - 1.61\ pK_a$ ($R^2 = 0.998$).

The intercepts (Table 4) obtained by extrapolation of the straight lines shown in Figure 1 to $\beta_2^H = 0.0$ correspond to log $k^0_{ArOH,A^{\bullet-}}/M^{-1}\ s^{-1}$ (see eq 8) and represent the nonmeasurable proton-transfer rate constants, $k^0/M^{-1}\ s^{-1}$, for the "free", non-hydrogen-bonded phenols in a hypothetical solvent which has "average" anion-solvating power but no hydrogen-bond accepting ability. The intercepts might be expected to correlate with the intrinsic driving force for the reaction, which must relate to the acidities of the phenol. This appears to be the case. In Figure 3, values of these β_2^H intercepts are shown plotted against the pK_a values of the phenols (see Table 2). Ignoring the outlying point for the intramolecularly hydrogen-bonded 2-methoxyphenol, a surprisingly good straight line ($R^2 = 0.998$) is obtained for the other five phenols, including even the di-ortho-substituted 2,4,6-trimethylphenol.[53] It would therefore appear that intramolecular hydrogen bonding of phenolic hydroxyl groups retards proton transfers just as it retards hydrogen-atom transfers.[19]

Conclusions and Predictions

Solvent effects on the rates of proton transfers from phenols to the anthracene radical anion yield better linear free-energy correlations when plotted against the β parameters of Taft and co-workers[15] than when plotted against the β_2^H parameters of Abraham et al.[6] Both β and β_2^H purport to be "clean" measures

(47) Note that the rate constants for 3,5-dichlorophenol in PC and MeCN are ca. 1% of the diffusion-controlled limiting values (cf. Tables 3 and 5). There is, therefore, only limited kinetic "space" for better than average anion solvation effects to manifest themselves for this phenol in these two solvents.

(48) See ref 13, p 432.

(49) In this connection, it has been pointed out[50] "that it is better to study one good model with precision than to take the average of results obtained from many poor models".

(50) Nicolet, P.; Laurence, C. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1071−1079.

(51) Kamlet, M. J.; Taft, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 377−383.

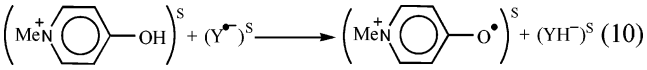
(52) This view is supported by the fact that HBD solvents are better anion solvators than dipolar aprotic solvents.[13] Furthermore, the β values for alcohols[15] are much larger than their β_2^H values.[6]

(53) This 5-point line is better than might have been expected in view of the fairly substantial standard deviations for the plots shown in Figure 1. For the six phenols, these standard deviations for the intercepts (and slopes, in parentheses) are 3,5-Cl_2, ±0.32 (±0.48); 4-CF_3, ±0.40 (±0.60); none, ±0.76 (±0.76); 4-MeO, ±0.93 (±0.71); 2,4,6-Me_3, ±0.44 (±0.73); 2-MeO, ±0.76 (±1.24). A related plot of the intercepts for these five phenols against Bordwell's[21] pK_{DMSO} values (Table 2) gives a notably poorer correlation ($R^2 = 0.909$), a result which causes us no surprise.[54]

of the relative HBA activities of organic bases. This is almost certainly true for β_2^H, but our results strongly imply that β values are "contaminated" by a contribution from anion solvation. *We therefore recommend that solvent effects on the rates of proton transfers should be correlated with* β_2^H *since the discovery of particular solvents in which the rates are faster or slower than expected will yield additional information about the reaction in question.*

KSEs on H-atom transfers between neutral molecules and neutral free radicals have been shown to be extremely well correlated by β_2^H [7] (provided there is no change in the reaction mechanism).[39a,b,55] We predict that KSEs for H-atom transfers between charged species will also be fairly well correlated by β_2^H *since there will be no charge migration between the reactants*, for example, reactions 9 and 10, with any deviations most probably arising from changes in the degree of *charge localization* between reactants and the transition state:

$$(\mathrm{ArOH})^S + (\mathrm{Y}^{\bullet -})^S \rightarrow (\mathrm{ArO}^{\bullet})^S + (\mathrm{YH}^-)^S \qquad (9)$$



(10)

Proton transfers necessarily involve charge migration. *Anion solvation effects* are likely to become important when negative charge migrates, particularly if the degree of localization of the charge changes significantly between the reactants and the transition states (which will frequently be similar to the changes between the reactants and products). This is the case for the reactions between phenols and the anthracene radical anion, where a highly delocalized negative charge migrates to become much more localized in the phenoxide anion:

$$(\mathrm{ArOH})^S + (\mathrm{A}^{\bullet -})^S \rightarrow (\mathrm{ArO}^-)^S + (\mathrm{AH}^{\bullet})^S \qquad (11)$$

As reported herein, the rate constants for reaction 1 in THF, a poor anion-solvating solvent, were always slower than expected (red points in Figure 1), whereas rate constants in the good anion solvating solvents, PC and MeCN, were faster than expected (green points in Figure 1). We predict that *anion solvation effects* would also be observed were the negative charge to become more delocalized in the transition state (or products) of some otherwise similar reaction, but that now THF would be a fast solvent while PC and MeCN would be slow solvents.

The rates of proton transfers that involve the migration of positive charge, e.g.

$$(\mathrm{XH}^+)^S + (\mathrm{Y})^S \rightarrow (\mathrm{X})^S + (\mathrm{YH}^+)^S \qquad (12)$$

are predicted to exhibit *cation solvation effects* if the charge becomes significantly more localized or delocalized during the reaction.

The foregoing predictions extend the rules relating to the effects of solvents on the rates of aliphatic nucleophilic substitution and elimination reactions formulated by Hughes and Ingold.[56−58] These rules are based on a simple, qualitative solution model which considers only pure electrostatic interactions between ions or dipolar molecules and the solvent in the initial and transition states. The rules can be summarized as follows.

An increase in solvent polarity will:

(i) Increase the rates of those reactions in which the charge density is greater in the transition state than in the reactant molecule(s).

(ii) Decrease rates when charge density is lower in the transition state than in the reactant(s).

(iii) Have a negligible effect on the rates when there is little or no change in the charge density between the transition state and reactant(s).

Hughes and Ingold treated the solvent as a dielectric continuum characterized by its relative permittivity, ϵ_r, or by its dipole moment, μ, or by its electrostatic factor, $\epsilon_r\mu$. Thus "solvent polarity" refers to the ability of a solvent to interact electrostatically with solute molecules.

The Hughes−Ingold rules[56−58] ignore hydrogen bonding, but it is H-bonding from the substrate to the solvent which controls KSEs for H-atom transfers[7] and dominates KSEs for proton transfers[1,2] (this work). The present extension of these rules is specific to these two classes of reaction. It is quantitative for H-atom transfers (thanks to the KSEs being controlled by H-bonding and therefore being correlated by Abraham et al.'s β_2^H values[6]). However, this extension is, as yet, only semi-quantitative for proton transfers. Nevertheless, solvents in which $\log k^S/\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ values for proton transfers are larger or smaller than those defined by the equation

$$\log k^S = \log k^0 - 8.3\,\alpha_2^H\,\beta_2^H \qquad (13)$$

(which must be based on rate measurements in a number of solvents with as wide a range in β_2^H as possible) provide information on the change in charge density between the transition state and reactants. For example, we have demonstrated that THF is a slow solvent for reactions in which negative charge becomes more localized on passing from the reactants to the products, and we have therefore predicted that THF will be a fast solvent when negative charge becomes less localized in a reaction. Additional studies on proton-transfer KSEs should provide sufficient insight to formulate *quantitative equations that will reliably predict reaction rates in any solvent* with the accuracy and generality of the H-atom transfer equation:

$$\log k^S_{\mathrm{XH,Y}\bullet} = \log k^0_{\mathrm{XH,Y}\bullet} - 8.3\,\alpha_2^H\,\beta_2^H \qquad (14)$$

XH = ArOH, $\mathrm{ArNH_2}$, ROOH, RH and $\mathrm{Y}^{\bullet}$ = $\mathrm{RO}^{\bullet}$, $\mathrm{ROO}^{\bullet}$, **dpph**$^{\bullet}$, $\mathrm{R}^{\bullet}$.

Experimental Section

The Reaction Scheme. In organic electrochemistry, the reaction between the anthracene radical anion and unsubstituted phenol in non-HBD solvents,[12] such as DMF and DMSO, provides a clear-cut example of the so-called DISP1 mechanism, that is, an example of a reaction following the pathway shown in Scheme 2 (where HB denotes the proton donor).

(54) See, for example: Pratt, D. A.; Blake, J. A.; Mulder, P.; Walton, J. C.; Korth, H.-G.; Ingold, K. U. *J. Am. Chem. Soc.* **2004**, *126*, 10667−10675 and references cited therein.
(55) Foti, M.; Daquino, C.; Geraci, C. *J. Org. Chem.* **2004**, *69*, 2309−2314.
(56) (a) Hughes, E. D.; Ingold, C. K. *J. Chem. Soc.* **1935**, 244−255. (b) Hughes, E. D. *Trans. Faraday Soc.* **1941**, *37*, 603−632. (c) Hughes, E. D.; Ingold, C. K. *Trans. Faraday Soc.* **1941**, *37*, 657−686.
(57) Ingold, C. K. *Structure and Mechanism in Organic Chemistry*, 2nd ed.; Cornell University Press: Ithaca, NY; pp 457−463 and pp 681−686.
(58) See ref 13, pp 163−173 and pp 215−217.

Scheme 2

$$A + e^- \rightleftharpoons A^{\bullet -}$$

$$A^{\bullet -} + HB \xrightarrow{k_{HB,A^{\bullet -}}} AH^{\bullet} + B^-$$

$$AH^{\bullet} + A^{\bullet -} \xrightarrow{k_{disp}} AH^- + A$$

$$AH^- + HB \xrightarrow{fast} AH_2 + B^-$$

The overall reaction involves the transfer of two electrons and two protons with the formation of 9,10-dihydroanthracene. The rate-determining step is protonation of the radical anion, $A^{\bullet -}$, leading to the neutral radical, $AH^{\bullet}$, which is more easily reduced than the starting anthracene, A, by several hundred millivolts.[59] The reduction of $AH^{\bullet}$ by disproportionation with $A^{\bullet -}$ can therefore be assumed to take place with a second-order rate constant (k_{disp}) close to that for a diffusion-controlled reaction which ensures that the proton-transfer step is essentially irreversible. The anion (AH^-) formed by reduction of $AH^{\bullet}$ is more basic than $A^{\bullet -}$ by several orders of magnitude,[59] and consequently, the second proton is transferred in a fast, irreversible reaction whenever a proton donor capable of protonating $A^{\bullet -}$ is present. The rate measured by electrochemical techniques therefore represents the protonation of the anthracene radical anion.

Electrochemical Measurements. Whenever possible, the apparent rates of protonation of $A^{\bullet -}$ by each phenol were measured at four concentrations of the phenol in each of the solvents using derivative cyclic voltammetry (DCV). DCV is a reversal technique in which a fraction of the radical anions initially formed is detected upon reversal of the scan direction. The rate with which the potential is scanned (ν) is adjusted in order to detect the same fraction of radical anion independently of the rate of the chemical reaction (in this case protonation) consuming the radical anion. This corresponds to a fixed value of R_I', which is the ratio of the heights of the peaks of the derivative of the voltammogram, $R_I' = -I'_{p,ox}/I'_{p,red}$.[60] For each solution, the value of $E^{\circ\prime}$ for anthracene ($E^{\circ\prime}$ is the formal potential of the $A/A^{\bullet -}$ couple) was determined with respect to the reference electrode (in the absence of any phenol) and the potential of scan reversal (E_{sw}) for DCV measurements set to $E^{\circ\prime} = -0.3$ V. For each phenol concentration, the scan rate in the DCV experiments was varied in order to obtain $R_I' = 0.5$ or $R_I' = 0.3$ (or both). In cases where the background reduction of the proton donor was visible, the switch potential for the DCV measurements was changed from $E^{\circ\prime} = -0.3$ V to $E^{\circ\prime} = -0.25$ V. When the reaction was too fast to obtain any of these ratios with scan rates less than 500 V s^{-1}, linear sweep voltammetry (LSV) measurements were used instead.

When the rate of proton transfer to $A^{\bullet -}$ is fast compared to the duration of the experiment, the voltammogram will be completely chemically irreversible, that is, no radical anion will be detected in the reverse scan. Under these conditions, the system is under purely kinetic control, and the steady-state approximation will apply to the radical anion concentration due to mutual competition of kinetics and diffusion. To ensure pure kinetic conditions, LSV measurements are carried out at low scan rates, and the quantity measured is the reduction peak potential with respect to $E^{\circ\prime}$ (obtained in the absence of proton donor), $E_p - E^{\circ\prime}$, as a function of scan rate (and proton donor concentration).

Procedure. For each solvent, the same (100 mL) batch of solvent containing 0.1 M n-Bu_4NPF_6 (except for THF, where 0.2 M n-Bu_4NPF_6 was used) and 1.0 mM anthracene was used for all measurements. In each solvent, 2.5 M stock solutions of each of the phenols were prepared immediately before the measurements were started. For each series of measurements, 5 or 10 mL of the solvent (0.1 M n-Bu_4NPF_6, 1.0 mM anthracene) was pipetted into the electrochemical cell. The solution was carefully bubbled with nitrogen (for solvents having high vapor pressures, the nitrogen was saturated with solvent before entering the cell) for at least 15 min. During all measurements, a slow stream of nitrogen was maintained above the solution. The stability of the anthracene radical anion in the absence of any phenol was checked by DCV measurements at low scan rates, and the value of $E^{\circ\prime}$ with respect to the reference electrode was determined. In cases where LSV measurements were to be made upon addition of the phenol, LSV measurements were also carried out on the anthracene solution using the same scan rates (0.2, 0.5, 1, 2, 5, and 10 V s^{-1}) as were later used after addition of the phenol. The LSV measurements were made with the range of scan rates mentioned above and using the procedure previously described.[61]

After measurements on the pure anthracene solution, phenol from the stock solution was added by a syringe in portions, giving solutions that were 10, 20, 40, and 80 mM in the phenol. After each addition and proper mixing by nitrogen bubbling, the DCV or LSV measurements (or both) were carried out. All measurements were done at room temperature (21 ± 1 °C) except for the measurements done using PC as solvent and 2,4,6-trimethylphenol, 2- and 4-methoxyphenol as the proton donors. In those three series of measurements, the temperature was 25 ± 1 °C. However, no correction for the change in temperature was made since the temperature effect on this type of reaction is modest.[62]

For 3,5-dichlorophenol, the proton-transfer reaction was so fast that DCV measurements were only possible in HMPA and at a single concentration in DMSO, and for 4-(trifluoromethyl)phenol only in HMPA and DMSO and at a single concentration in TEP. For these two phenols, the rate constants were therefore mainly based on LSV (vide infra). In addition, for these, the two most acidic phenols, proton reduction seriously interfered with the measurements in MeCN at the higher phenol concentrations, and therefore, the LSV measurements were carried out only at the lowest phenol concentrations. In HMPA, the reactions were so slow that unidentified background reactions excluded the use of this solvent for all phenols except 3,5-dichlorophenol and 4-trifluoromethylphenol.

Calculation of the Apparent Second-Order Rate Constants from DCV Measurements. Conversions of the experimentally determined $\nu_{0.5}$ or $\nu_{0.3}$ values, that is, the values of the scan rate necessary to obtain $R_I' = 0.5$ or $R_I' = 0.3$, to rate constants were done using simulated data for the DISP1 mechanism with the appropriate value of $E_{sw} - E^{\circ\prime}$ and the correct stoichiometry as imposed by the formation of homoconjugation complexes. Since the formation of the homoconjugation complex between the phenol and its conjugate base takes place in competition with hydrogen bonding between the phenol and the solvent, the apparent equilibrium constant for formation of the homoconjugation complex increases with decreasing values of β_2^H for the solvents.[2] The equilibrium constants in DMSO for formation of homoconjugation complexes for a series of phenols are very similar and close to 2×10^3 M^{-1}.[63] This value of the equilibrium constant was therefore chosen for all the phenols in DMSO, except for 2-methoxyphenol. In the solvents with lower β_2^H values, the homoconjugation was treated as an irreversible reaction since the deviations between an irreversible reaction and a reaction with an equilibrium constant $>3 \times 10^3$ M^{-1} are negligible.[1] The intramolecular hydrogen bond in 2-methoxyphenol lowers the ability of this phenol to act as a hydrogen bond donor (cf. α_2^H for this phenol in Table 2), and the stoichiometric effect of homoconjugation was therefore ignored for 2-methoxyphenol in all solvents. Using the proper simulated data for each combination of solvent and phenol, a rate constant was calculated at each value of C^o_{ArOH}.

(59) Parker, V. D.; Tilset, M.; Hammerich, O. *J. Am. Chem. Soc.* **1987**, *109*, 7905−7906.
(60) Ahlberg, E.; Parker, V. D. *Acta Chem. Scand.* **1980**, *B34*, 97−102.
(61) Nielsen, M. F.; Hammerich, O.; Parker, V. D. *Acta Chem. Scand.* **1986**, *B40*, 101−118.
(62) Nielsen, M. F. Unpublished results.
(63) Bordwell, F. G.; McCallum, R. J.; Olmstead, W. N. *J. Org. Chem.* **1984**, *49*, 1424−1427.

Calculation of the Apparent Second-Order Rate Constants from LSV Measurements. Since these data were all obtained in cases where the proton-transfer reaction was very fast, the reactions do not necessarily follow the DISP1 mechanism. When the rate of the proton transfer to $A^{\bullet-}$ increases, the width of the reaction layer in which $AH^{\bullet}$ is formed decreases, and competition between reduction in solution by $A^{\bullet-}$ (DISP1) and diffusion of $AH^{\bullet}$ back to the electrode followed by reduction at the electrode surface becomes important. When the disproportionation step in Scheme 2 is replaced with reduction of $AH^{\bullet}$ at the electrode surface, the mechanism is denoted as ECE. The competition between the DISP1 and the ECE mechanisms has previously been analyzed in detail.[64−66]

Under the steady-state conditions present during the LSV measurements, the value of a single parameter (P) describes the competition between the ECE and the DISP1 mechanisms.[64] The parameter P is defined in eq 15, where (C_A^o) and (C_{HB}^o) denote, respectively, the stoichiometric concentrations of the substrate (anthracene) and the proton donor (a phenol). The rate constants are defined in Scheme 2, and in eq 15, the superscript S indicates the solvent in which the reaction takes place.

$$P = \frac{k_{disp}^S}{(k_{HB,A^{\bullet-}}^S)^{3/2}} \cdot \left(\frac{F\nu}{RT}\right)^{1/2} \cdot \frac{C_A^o}{(C_{HB}^o)^{3/2}} \quad (15)$$

Transition between the ECE and DISP1 mechanisms takes place over a range of approximately 2 orders of magnitude of P; when $P < 0.1$, the reaction can be considered to follow exclusively the ECE mechanism, whereas when $P > 10$, it can be considered to follow exclusively the DISP1 mechanism. For these two limiting mechanisms, eqs 16 and 17 give the relationship between the kinetic shift of the peak potential ($E_p - E^{o\prime}$) measured by LSV and the value of the second-order rate constant, $k_{HB,A^{\bullet-}}^S$, for the proton-transfer reaction as a function of the sweep rate and the stoichiometric concentration of the proton donor, C_{HB}^o (with the implicit assumption that $C_{HB}^o \gg C_A^o$). Combination of the two equations shows that the maximum error in the rate constant associated with application of the "wrong" formula for a particular reaction is a factor of 2 (eq 18).

$$\text{ECE:} \quad E_p - E^o = -0.78\frac{RT}{F} + \frac{RT}{2F}\ln\left(\frac{C_{HB}^o \times k_{HB,A^{\bullet-}}^S RT}{F\nu}\right) \quad (16)$$

$$\text{DISP1:} \quad E_p - E^o = -0.78\frac{RT}{F} + \frac{RT}{2F}\ln\left(\frac{C_{HB}^{o\,2} k_{HB,A^{\bullet-}}^S RT}{F\nu}\right) - \frac{RT}{2F}\ln 2 \quad (17)$$

$$\frac{k_{HB,A^{\bullet-}}^S(\text{DISP1})}{k_{HB,A^{\bullet-}}^S(\text{ECE})} = 2 \quad (18)$$

Equations 16 and 17 are both based on uncomplicated Nernstian behavior of the initial heterogeneous electron-transfer process, that is, the electron transfer behaves as an equilibrium process. Despite the fact that the standard heterogeneous electron-transfer rate constant, k_{het}^0/cm s^{-1}, for anthracene is fairly large (a value of 1.6 cm s^{-1} in DMF has been reported[67]), a fast follow-up reaction of the radical anion will lead to a considerable anodic shift of the reduction peak (as evident from eqs 16 and 17). The effects of the potential on the magnitude of the heterogeneous electron transfer rate constants in the forward and backward directions are given by the Butler−Volmer expression, eq 19a−b, where α is the transfer coefficient (which for anthracene is close to 0.5):

$$k_f = k_{het}^0 \exp[-\alpha(E - E^\circ)F/(RT)] \quad (19a)$$

$$k_b = k_{het}^0 \exp[(1-\alpha)(E - E^\circ)F/(RT)] \quad (19b)$$

For the fast reactions studied by LSV in the present work, a shift of the peak potential, E_p, from $E_p = E^{o\prime} - 28.5$ mV in the absence of follow-up reactions to $E_p \approx E^{o\prime} + 100$ mV in the fast proton-transfer reaction, corresponds to a decrease in k_f by more than a factor of 12. The decrease in k_f may cause shifts in the measured values of E_p compared to the values that would have been obtained had the electron transfer been truly Nernstian. This shift will—independently of whether the reaction follows the DISP1 or the ECE scheme—lead to values of the calculated $k_{HB,A^{\bullet-}}^S$, which are artificially too low.

Rather than accepting the uncertainties introduced by assuming Nernstian electron transfer and neglecting the gradual transitions from DISP1 to ECE in the calculation of $k_{HB,A^{\bullet-}}^S$ from LSV data, it was decided to simulate the full reaction scheme (parallel electron transfer in solution and at the electrode surface) for each combination of solvent and phenol at each concentration of the phenol using best estimates of k_{het}^0, k_{disp}, and D_A (the diffusion coefficient for anthracene and its radical anion) for each of the solvents.

The second-order rate constant, k_{disp}^S, for the disproportionation reaction in Scheme 2 can, as mentioned, be approximated with the second-order rate constant for a diffusion-controlled reaction in the same solvent, k_{diff}^S. The values of k_{diff}^S for the different solvents can be calculated from the Smoluchowski eq 20, using the viscosities given in Table 1. These k_{diff}^S values are given in Table 5.

$$k_{diff}^S/\text{M}^{-1}\,\text{s}^{-1} = 8\,RT/(3\eta^S) \quad (20)$$

The Walden rule, eq 21, derived from the Stokes−Einstein equation, allows calculation of the diffusion coefficient of anthracene in solvent S2, D_A^{S2}, from a known value in solvent S1, D_A^{S1}, using again the viscosity values from Table 1. The value of $D_A^{DMF} = 8.40 \times 10^{-6}$ cm^2 s^{-1} [68] was used as D_A^{S1}, and the calculated values of D_A^{S2} for the other solvents are given in Table 5.

$$D_A^{S1}\,\eta^{S1} = D_A^{S2}\,\eta^{S2} \quad (21)$$

The value of the standard heterogeneous electron-transfer rate constant is also solvent dependent, and values of $k_{het}^{0,S}$ were estimated from eq 22 in which τ_L^S is the longitudinal relaxation time of the solvent S, assuming that the solvent dependence can be described by eq 23, as previously found for systems with small internal reorganization

Table 5. Estimated Values of k_{diff}^S, D_A^S, and $k_{het}^{0,S}$ in Seven of the Solvents Used in This Work

solvent[a]	$10^{-9}\,k_{diff}^S$/M^{-1} s^{-1} [b]	$10^6\,D_A^S$/cm^2 s^{-1} [c]	τ_L^S/ps[d]	$k_{het}^{0,S}$/cm s^{-1} [e]
DMSO	3.3	3.4	2.1	0.84
TEP	3.1	3.1	-	1.5[f]
DMF	8.2	8.4	1.1	1.6
THF	14	15	1.7	1.0
acetone	22	22	0.3	5.8
PC	2.6	2.7	1.7	1.0
MeCN	19	20	0.2	8.0

[a] The abbreviations are defined in the text. HMPA is not included since only slow reactions were studied (by DCV) in this solvent. [b] Calculated from eq 20. [c] Calculated from eq 21 using $D_A^{DMF} = 8.40 \times 10^{-6}$ cm^2 s^{-1} from ref 68. [d] Longitudinal relaxation times, τ_L^S, were taken from ref 69. [e] Calculated from eq 22 and used in simulations of LSV experiments. [f] Estimated from the experimental data.

(64) Amatore, C.; Savéant, J.-M. *J. Electroanal. Chem.* **1977**, *85*, 27−46.
(65) Amatore, C.; Savéant, J.-M. *J. Electroanal. Chem.* **1979**, *102*, 21−40.
(66) Amatore, C.; Gareil, M.; Savéant, J.-M. *J. Electroanal. Chem.* **1983**, *147*, 1−38.
(67) Andrieux, C. P.; Delgado, G.; Savéant, J.-M.; Su, K. B. *J. Electroanal. Chem.* **1993**, *348*, 107−121.

energies[69] and using the cited value[67] of $k_{het}^{0,DMF} = 1.6$ cm s^{-1} as $k_{het}^{0,S1}$ for anthracene.

$$k_{het}^{0,S2} = k_{het}^{0,S1} \cdot \frac{\tau_L^{S1}}{\tau_L^{S2}} \quad (22)$$

$$\ln k_{het}^{0,S} = \text{constant} - \ln \tau_L^S \quad (23)$$

For each phenol concentration, the value of $k_{ArOH,A\bullet-}^S$ was then varied in the simulations to obtain the best over-all fit between the measured and the simulated values of $E_p - E^{o\prime}$ for each of the (normally six) scan rates applied. Owing to the visible contribution from proton reduction to the background in several cases, the half-peak width, $E_{p/2} - E_p$, tended to increase with increasing phenol concentration, and therefore, no attempts were made to match the experimentally determined half-peak widths with the simulations.

Correction for Contribution from a Dimer. Having determined the apparent second-order rate constant at each concentration of the phenol for every combination of phenol and solvent as explained above, it was obvious in some cases that the rate constants steadily increased with increasing concentration of the phenol. Those data were plotted according to eq 24 as previously described,[1] and the intercept was used as the best value of $k_{ArOH,A\bullet-}^S$, that is, the second-order rate constant pertaining to the monomer as the proton donor.

$$k_{obs}^S = k_{ArOH,A\bullet-}^S + k_{(ArOH)_2,A\bullet-}^S \cdot C_{ArOH}^o \quad (24)$$

Chemicals. The solvents *N*,*N*,*N*,*N*,*N*,*N*-hexamethylphosphortriamide (Aldrich, >97%), triethyl phosphate (Aldrich, 99%), dimethyl sulfoxide (Fluka, >99.5%), *N*,*N*-dimethylformamide (LabScan, HPLC grade), tetrahydrofuran (LabScan, HPLC grade), acetone (Aldrich, >99.9%), propylenecarbonate (Aldrich, GC grade), and acetonitrile (LabScan, 99.9%) were used as received or passed through a column of alumina (Woelm, W200) prior to use. The supporting electrolyte, tetra-*n*-butylammonium hexafluorophosphate (*n*-Bu_4NPF_6) (Aldrich), anthracene (Purelabo), and the phenols (Aldrich): phenol, 2,4,6-trimethylphenol, 2- and 4-methoxyphenol, 4-(trifluoromethyl)phenol, and 3,5-dichlorophenol, were used as received.

Cells, Electrodes, and Instrumentation. The cells and electrodes were identical to those previously described.[61] For each solvent, a new pseudo-reference electrode containing the actual solvent (with 0.1 M *n*-Bu_4NPF_6) in its interior was made up some days in advance in order to obtain a stable reference. No attempts were made to calibrate the reference electrodes with respect to a common potential scale. In all cases, the pseudo-reference electrode was stable to within a couple of millivolts during a series of measurements. The Hg working electrode was used in order to suppress direct proton reduction. The electrochemical equipment was essentially identical to that previously described,[70] except that in some of the measurements, the Nicolet Oscilloscope was replaced by a Tektronix RTD 710A digitizer. Locally developed software (in TransEra HT-Basic 7.2 under Windows 95) was used for instrument control and data treatment.

Digital Simulations. All simulations of DCV and LSV experiments were done using locally developed software and the methods previously described.[71]

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Supporting Information Available: Table S1. Detailed experimental conditions for each set of measurements used for calculation of the rate constants given in Table 3, and complete ref 31. This material is available free of charge via the Internet at http://pubs.acs.org.

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(68) Andrieux, C. P.; Garreau, D.; Hapiot, P.; Pinson, J.; Savéant, J.-M. *J. Electroanal. Chem.* **1988**, *243*, 321−335.
(69) Fawcett, W. R.; Foss, C. A. *J. Electroanal. Chem.* **1989**, *270*, 103−118.
(70) Nielsen, M. F.; Laursen, S. A.; Hammerich, O. *Acta Chem. Scand.* **1990**, *44*, 932−943.
(71) Andersen, M. L.; Nielsen, M. F.; Hammerich, O. *Acta Chem. Scand.* **1995**, *49*, 503−514.