

The Effect of Hydrogen Bonding between Methyl-Substituted Phenols and Dipolar Aprotic Solvents on the Rate Constants for Protonation of Anthracene Anion Radical

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The kinetics for the protonation of anthracene anion radical ($A^{\cdot-}$) by phenol and 13 methyl-substituted phenols (ArOH) have been studied by derivative cyclic voltammetry in dimethyl sulfoxide, *N,N*-dimethylformamide, propylene carbonate and acetonitrile. The observed rate constants were corrected for the stoichiometric effects of formation of the homoconjugation complexes, ArOH/ArO $^-$ and ArOH/ArOH/ArO $^-$ and the kinetic contributions from protonation of $A^{\cdot-}$ by ArOH dimers.

Available data for equilibrium (I) show that ArOH exists in solution predominantly as the ArOH/solvent hydrogen bond complex with only minor amounts of the 'free' ArOH present. It is suggested that the protonation of $A^{\cdot-}$ involves only the free ArOH in the proton transfer step (II). The unique rate constants corrected for the effect of equilibrium (I) were between two and three orders of magnitude higher than those usually referred to as the second-order rate constants for protonation of $A^{\cdot-}$.



The kinetic effect of methyl substituents in the 2,6-positions of the phenol was observed to depend on the solvent. It was found that these effects could be satisfactorily accounted for by the influence of the 2,6-methyl substituents on the magnitude of K_1 .

The 'best' values of the substituent constants, σ_2^+ and $\sigma_{2,6}^+$, defined by the protonation of $A^{\cdot-}$ were found to be between those defined by equilibrium (I) and those defined by the unique equilibrium acidity of the phenols. This is taken as an indication that the phenol O–H bond is stretched considerably in the transition state for protonation of $A^{\cdot-}$.

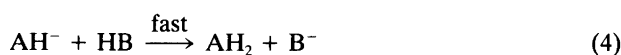
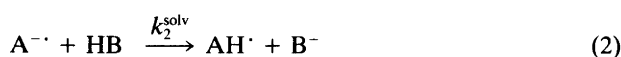
From the relation between k_{II} and ΔG° it was found that the Brønsted α value for the process is close to 0.5.

Although the mechanism for protonation of anion radicals derived from aromatic hydrocarbons in dipolar aprotic solvents is now well established^{1–14} with rate constants reported for a large number of cases,^{4,6,8–11,13–19} no systematic studies have been published aimed at the interpretation of the observed rate constants at the microscopic level. Such studies are of interest for two major reasons. (1) The general understanding of proton transfer reactions in dipolar aprotic solvents is much less detailed with respect to the microscopic steps than the understanding of proton transfer reactions in water and other hydroxylic media and (2) the characterization of anion radicals as bases from both a thermodynamic and a kinetic point of view is still fragmentary.

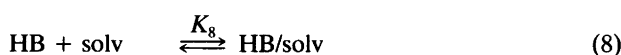
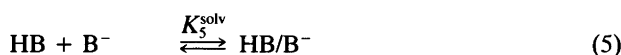
The purpose of the present paper is to present a detailed analysis of a new set of kinetic data for the protonation of anthracene anion radical by a series of closely related proton donors, phenol (PhOH) and 13 different methyl-substituted phenols in four dipolar aprotic solvents, dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF), propylene carbonate (PC) and acetonitrile (MeCN). Anthracene anion radical was chosen as the common anion radical because of its frequent use^{1–16,19,20} as a model substrate in protonation studies. The limitation of the proton donors to methyl-substituted phenols offers several advantages: (1) methyl substitution is unlikely to result in specific solvation effects caused by the substituent, (2) the interaction between substituents in neighboring positions is small²¹ and (3) methyl substitution will not affect the electrochemical inertness of the phenol in the potential range of interest.

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The general reaction scheme for formation of the product (AH_2) from the aromatic hydrocarbon (A) and the proton donor (HB) is given by reactions (1)–(4) with



(2) being rate determining. In addition, HB participates in several parallel hydrogen bonding equilibria including homoconjugation between the anion, B^- , and one, eqn. (5), or two, eqn. (6), molecules of HB, formation of the dimer, HB/HB, eqn. (7), and hydrogen bonding between the solvent and HB, eqn. (8), and HB/HB, eqn. (9). Here and in the following a slash, '/', indicates a hydrogen bond and the superscript 'solv' used in eqns. (2) and (5)–(7) refers to the observed value of the rate constant, k_i , or the equilibrium constant, K_i , for reaction (i) in the solvent 'solv'.



We have previously shown that the formation of the homoconjugation complex, HB/ B^- , eqn. (5), may affect the kinetic data for reactions (1)–(4) owing to changes in the stoichiometry of the overall reaction.^{12–14,20} In addition, we have observed that if the proton donor is capable of forming strong intramolecular hydrogen bonds, the observed kinetics are much less affected by a change from one dipolar aprotic solvent to another compared with the situation in which intramolecular hydrogen bond formation is impossible.²⁰ The strong solvent dependence observed in the latter case may be attributed to differences in the hydrogen bond interactions between the proton donor and the solvent, but these effects have not yet been systematically investigated.

In the analysis to follow, the effect of the hydrogen bonding equilibria, (5)–(9), will be evaluated. An attempt to correct the measured rate constants for the contributions from eqns. (5)–(9) will be made, the ultimate goal being to

gain insight into the rates of the microscopic proton transfer steps as well as the effects of solvent and substituents on the microscopic rate constants. The required hydrogen bonding equilibrium constants were estimated by application of a general approach recently described.²²

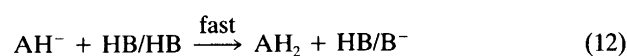
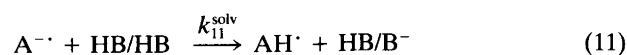
Results and discussion

All the kinetic data were obtained by derivative cyclic voltammetry (DCV) because of the high precision and wide kinetic range of this technique.²³ The measurements were carried out at 25 °C with $C_A^\circ = 1.0$ mM (A: anthracene) and $C_{HB}^\circ = 10, 20, 40$ and 80 mM (HB: the proton source) and involved recording of v_x with $x = 0.5$ for the reactions studied in DMSO and DMF, and $x = 0.3$, corresponding to a higher degree of conversion,¹³ for the faster reactions in PC and MeCN (see the Experimental section).

The experimental data. The simple mechanism, eqns. (1)–(4), results in rate law (10), which is first order in the anion radical concentration and first order in the proton source concentration.

$$-\frac{d[A^{\cdot-}]}{dt} = 2k_2^{\text{solv}}[A^{\cdot-}][\text{proton source}] \quad (10)$$

For $C_{HB}^\circ \gg C_A^\circ$ the rate law degenerates to the corresponding pseudo-first-order expression and we have shown¹³ that the lower limit of C_{HB}°/C_A° necessary for the assumption of pseudo-first-order conditions to be valid increases significantly when the formation of the HB/ B^- homoconjugation complex, eqn. (5), has to be included in the reaction scheme. Deviations from pseudo-first-order conditions caused by the stoichiometric effects of homoconjugation, eqns. (5) and (6), or kinetic contributions from the HB dimer in the proton transfer steps, eqns. (11) and (12), are reflected in the apparent reaction order in the proton source defined as the slope, $d \log v_x / d \log C_{HB}^\circ$, of the linear regression line determined by a particular set of $\log C_{HB}^\circ$ and $\log v_x$ values. However, we wish to emphasize that deviations from pseudo-first-order conditions and/or kinetic contributions from protonation of $A^{\cdot-}$ by the HB dimer predict a non-linear relationship between $\log C_{HB}^\circ$ and $\log v_x$ and consequently, the magnitude of the slope is not directly related to the reaction order in the proton source but serves merely as a diagnostic parameter.



The experimental values of $v_{0.5}$ and $v_{0.3}$ at $C_{HB}^\circ = 10$ mM for the 14 phenols in all four solvents are given in Table 1 together with the apparent reaction orders, $d \log v_x / d \log C_{HB}^\circ$.

Table 1. Values of $\nu_{0.5}$ or $\nu_{0.3}$ and the apparent reaction orders, $d \log \nu_x / d \log C_{\text{HB}}^{\circ}$, for the protonation of anthracene anion radical by phenol and methyl-substituted phenols in DMSO, DMF, PC and MeCN.^a

Phenol substituent	DMSO		DMF		PC		MeCN	
	$\nu_{0.5}/V \text{ s}^{-1}$	$\frac{d \log \nu_{0.5}}{d \log C_{\text{HB}}^{\circ}}$	$\nu_{0.5}/V \text{ s}^{-1}$	$\frac{d \log \nu_{0.5}}{d \log C_{\text{HB}}^{\circ}}$	$\nu_{0.3}/V \text{ s}^{-1}$	$\frac{d \log \nu_{0.3}}{d \log C_{\text{HB}}^{\circ}}$	$\nu_{0.3}/V \text{ s}^{-1}$	$\frac{d \log \nu_{0.3}}{d \log C_{\text{HB}}^{\circ}}$
None	6.90	1.06	12.3	1.22	59.0	1.00 ^b	124	1.09 ^b
2-Methyl	3.12	1.00	6.67	1.11	20.4	1.09	58.2	1.06
3-Methyl	5.00	1.01	8.06	1.25	32.2	1.10	97.5	1.18
4-Methyl	2.95	1.09	4.55	1.27	24.2	1.11	56.2	1.26
2,3-Dimethyl	1.87	1.01	3.52	1.17	10.1	1.17	31.5	1.20
2,4-Dimethyl	1.60	1.03	2.52	1.14	7.11	1.26	25.2	1.20
2,5-Dimethyl	2.65	0.99	3.96	1.16	15.0	1.18	41.3	1.19
2,6-Dimethyl	2.80	1.01	4.77	1.12	8.54	1.07	25.9	1.10
3,4-Dimethyl	2.11	1.08	3.32	1.24	10.6	1.38	42.6	1.32
3,5-Dimethyl	3.36	1.06	6.69	1.27	23.5	1.18	63.9	1.26
2,3,5-Trimethyl	1.92	0.99	2.45	1.22	6.50	1.23 ^b	23.5	1.22
2,3,6-Trimethyl	2.29	0.95	3.53	1.06	5.39	1.08	12.2	1.11
2,4,6-Trimethyl	1.48	0.96	2.94	1.16 ^b	2.77	1.18	6.75	1.11
3,4,5-Trimethyl	2.01	1.11 ^b	2.50	1.38 ^b	6.28	1.70 ^b	37.2	1.37 ^b

^aValues of $\nu_{0.5}$ and $\nu_{0.3}$ measured at $C_{\text{A}}^{\circ} = 1.0 \text{ mM}$ and $C_{\text{HB}}^{\circ} = 10 \text{ mM}$ and values of $d \log \nu_x / d \log C_{\text{HB}}^{\circ}$ based on measurements at $C_{\text{HB}}^{\circ} = 10, 20, 40$ and 80 mM . Supporting electrolyte: Bu_4NPF_6 (0.1 M); $T = 25 \text{ }^{\circ}\text{C}$. ^bBased on ν_x at $C_{\text{HB}}^{\circ} = 10, 20$ and 40 mM .

Correction for the effects of homoconjugation, eqns. (5) and (6). Although $\nu_{0.5}$ and $\nu_{0.3}$ are both proportional to the apparent rate constant, the constants of proportionality are different owing to the different degrees of conversion involved. Thus, in order to make a direct comparison of the rates of the 4×14 proton transfer reactions the experimental values of $\nu_{0.5}$ and $\nu_{0.3}$ have to be converted into rate constants. This requires information about K_5^{solv} and K_6^{solv} for the homoconjugation equilibria, eqns. (5) and (6).

As demonstrated recently²² it is possible for a given pair, HB, B⁻, to estimate the value of the equilibrium constant for homoconjugation in the solvent sol_2 , $K_5^{\text{sol}_2}$, from a known value of the equilibrium constant, $K_5^{\text{sol}_1}$, measured in a different solvent, sol_1 , provided that the equilibrium constants, K_8 , for the formation of HB/ sol_1 and HB/ sol_2 are known. The approach is based on the assumption that each HB molecule can act as hydrogen bond donor to only one base at a time and on the existence of 'unique' equilibrium constants, K_5 and K_8 , essentially independent of solvent, for formation of HB/B⁻ and HB/ sol_v . It follows that the numerical values of $K_5^{\text{sol}_v}$ (and $K_6^{\text{sol}_v}$) in a given solvent is then the result of competition between the hydrogen bonding equilibria (5), (6) and (8).²²

On the basis of the estimates of the unique equilibrium constants, K_5 , for homoconjugation²² (Table 2) for the methyl-substituted phenols, approximate values of $K_5^{\text{sol}_v}$ (Table 2) were calculated from eqn. (13) for the 14 phenols in DMSO, DMF, PC and MeCN using the values of K_8 (Table 3) reported earlier.²²

$$K_5^{\text{sol}_v} = K_5 / (1 + K_8[\text{sol}_v]) \quad (13)$$

Values of $K_6^{\text{sol}_v}$ can only be estimated owing to the lack of

primary data. The equilibrium constant for the overall formation of a two-to-one homoconjugation complex has been reported only for PhOH in MeCN²⁴ from which $K_6^{\text{MeCN}} = 50 \text{ M}^{-1}$ can be calculated. However, from the data given in Ref. 22 it can be estimated that the values of K_6^{DMSO} and K_6^{DMF} are less than 10 M^{-1} for all the phenols, whereas the values of K_6^{PC} and K_6^{MeCN} for phenols having unsubstituted *ortho* positions are in the range $50\text{--}100 \text{ M}^{-1}$. For the *ortho*-substituted phenols, K_6^{PC} and K_6^{MeCN} were estimated to be less than 10 M^{-1} .²²

We have shown earlier²⁵ that formation of the homoconjugation complex for PhOH may be treated kinetically as a fast and reversible process during protonation of A⁻ in DMSO. Application of Bordwell's value,²⁶ $2.3 \times 10^3 \text{ M}^{-1}$, for K_5^{DMSO} resulted in constant values of k_2^{DMSO} over a wide range of C_{HB}° . From Table 2 it is seen that K_5^{DMSO} varies little with the structure of the phenol and consequently, it was decided to use the value for PhOH for the methyl-substituted compounds in the calculations of k_2^{DMSO} . The theoretical data obtained by digital simulation for mechanism (1)–(5) with (5) as a fast equilibrium process was used for all the phenols in DMSO.

Theoretical DCV data for mechanism (1)–(4) followed by fast and irreversible (5) and for mechanism (1)–(5) with (5) being an equilibrium process show that the difference in the proportionality constants to be used in the conversion of ν_x into rate constants amounts to less than 0.2% for $K_5^{\text{sol}_v} > 3 \times 10^3 \text{ M}^{-1}$. Thus, for the data obtained in DMF, PC and MeCN it was decided to apply the theoretical data to mechanism (1)–(4) followed by irreversible (5).

For phenols having unsubstituted *ortho* positions the values of $K_6^{\text{sol}_v}$ given in the footnote to Table 4 (see later) were used for PC and MeCN. For the 2-methyl and 2,6-

Table 2. Estimated and literature values of the equilibrium constant for homoconjugation, K_5^{solv} , for phenol and methyl-substituted phenols in four dipolar aprotic solvents.

Phenol substituent	K_5/M^{-1} ^a	$K_5^{\text{DMSO}}/\text{M}^{-1}$	$K_5^{\text{DMF}}/\text{M}^{-1}$ ^b	$K_5^{\text{PC}}/\text{M}^{-1}$ ^b	$K_5^{\text{MeCN}}/\text{M}^{-1}$ ^b
None	6.8×10^6	2.3×10^3 ^c	7.0×10^3	6.3×10^4	6.9×10^4
2-Methyl	2.2×10^6	1.4×10^3 ^c	3.9×10^3	3.0×10^4	3.1×10^4
3-Methyl	5.2×10^6	2.3×10^3 ^c	6.7×10^3	5.6×10^4	5.9×10^4
4-Methyl	5.6×10^6	2.5×10^3 ^c	7.2×10^3	6.1×10^4	6.4×10^4
2,3-Dimethyl	2.0×10^6 ^d	1.7×10^3 ^b	4.5×10^3	3.3×10^4	3.2×10^4
2,4-Dimethyl	2.0×10^6 ^d	1.7×10^3 ^b	4.5×10^3	3.4×10^4	3.2×10^4
2,5-Dimethyl	2.0×10^6 ^d	1.6×10^3 ^b	4.3×10^3	3.2×10^4	3.1×10^4
2,6-Dimethyl	6.4×10^5	1.9×10^3 ^c	4.1×10^3	2.3×10^4	2.0×10^4
3,4-Dimethyl	5.5×10^6 ^d	3.5×10^3 ^b	9.7×10^3	7.5×10^4	7.6×10^4
3,5-Dimethyl	5.5×10^6 ^d	3.0×10^3 ^b	8.5×10^3	6.8×10^4	7.1×10^4
2,3,5-Trimethyl	2.0×10^6 ^d	2.0×10^3 ^b	5.2×10^3	3.6×10^4	3.5×10^4
2,3,6-Trimethyl	6.0×10^5 ^d	2.2×10^3 ^b	4.8×10^3	2.5×10^4	2.0×10^4
2,4,6-Trimethyl	6.0×10^5 ^d	2.5×10^3 ^b	5.2×10^3	2.7×10^4	2.2×10^4
3,4,5-Trimethyl	5.5×10^6 ^d	3.9×10^3 ^b	1.1×10^4	8.1×10^4	8.1×10^4

^a $K_5 = K_5^{\text{DMSO}}/(1 + K_8[\text{DMSO}])$, K_8 taken from Table 3. ^b $K_5^{\text{solv}} = K_5/(1 + K_8[\text{solv}])$, K_8 taken from Table 3. ^c From Ref. 26. ^d From Ref. 22.

dimethyl substituted phenols in PC and MeCN and for all the phenols in DMSO and DMF the K_6^{solv} values were so small that corrections were deemed unnecessary.

The values of the second-order rate constant, $k_{\text{obs}}^{\text{solv}}$, calculated as indicated above from the $\nu_{0.5}$ and $\nu_{0.3}$ values obtained at $C_{\text{HB}}^{\circ} = 10$ mM are summarized in Table 4 together with the reaction orders in the proton source, $1 + d \log k_{\text{obs}}^{\text{solv}}/d \log C_{\text{HB}}^{\circ}$.

When DMSO is the solvent, the reaction orders are in the range 0.90–1.04 whereas the reaction orders for the three other solvents with only two exceptions are within the range 1.00–1.60. As discussed in the Experimental section the experimental errors in the measurements of this study are somewhat larger than those in some of our previous

protonation studies^{13,25} and for this reason only deviations from unity larger than ± 0.1 are considered significant. With these limitations in mind the data in Table 4 show that deviations from first-order behavior are found in DMF for 8 phenols, in PC for 6 phenols and in MeCN for 8 phenols. In all these cases the values of $k_{\text{obs}}^{\text{solv}}$ increase with increasing phenol concentration.

Correction for kinetic contributions from the hydrogen-bonded dimer. From a kinetic point of view protonation of A^- by a hydrogen-bonded dimer is more serious than the essentially stoichiometric effects of the homoconjugation equilibria, (5) and (6). With reactions (11) and (12) included in the reaction scheme rate law (14) applies assuming that the steady state assumptions for AH^+ and AH^- are still valid.

$$-\frac{d[\text{A}^-]}{dt} = 2[\text{A}^-](k_2^{\text{solv}}[\text{monomer}] + k_{11}^{\text{solv}}[\text{dimer}]) \quad (14)$$

The estimated magnitudes of the K_7^{solv} values²² show that the total amount of dimer at C_{HB}° up to 100 mM never exceeds 5% in any of the four solvents and accordingly, we have $C_{\text{HB}}^{\circ} \approx [\text{monomer}]$ and the observed second-order rate constant, $k_{\text{obs}}^{\text{solv}}$ (Table 4), may then be written as eqn. (15).

$$k_{\text{obs}}^{\text{solv}} = k_2^{\text{solv}} + k_{11}^{\text{solv}} K_7^{\text{solv}} C_{\text{HB}}^{\circ} \quad (15)$$

The most convenient way to separate the monomer and dimer contributions is to plot $k_{\text{obs}}^{\text{solv}}$ vs. C_{HB}° , which, according to eqn. (15), is predicted to define a straight line of intercept k_2^{solv} and slope, $k_{11}^{\text{solv}} K_7^{\text{solv}}$. The values of the second-order rate constants for proton transfer from the monomer, k_2^{solv} , obtained in this way for reactions with reaction orders larger than 1.1 are given in Table 5. When the reaction order was less than 1.1 the values of k_2^{solv} were determined

Table 3. Values of the unique equilibrium constant for hydrogen bond formation, K_8 , for phenol and methyl-substituted phenols in four dipolar aprotic solvents.^a

Phenol substituent	K_8/M^{-1}			
	DMSO	DMF	PC	MeCN
None	210	75	9.2	5.1
2-Methyl	112	44	6.2	3.7
3-Methyl	160	60	7.8	4.5
4-Methyl	160	60	7.7	4.5
2,3-Dimethyl	84	34	5.1	3.2
2,4-Dimethyl	82	34	5.0	3.2
2,5-Dimethyl	89	36	5.3	3.3
2,6-Dimethyl	24	12	2.3	1.6
3,4-Dimethyl	110	44	6.2	3.7
3,5-Dimethyl	130	50	6.8	4.0
2,3,5-Trimethyl	71	30	4.6	2.9
2,3,6-Trimethyl	19	9.7	2.0	1.5
2,4,6-Trimethyl	17	8.8	1.8	1.4
3,4,5-Trimethyl	99	40	5.7	3.5

^a From Ref. 22. It is assumed that $K_8 = K_8^{\text{CCl}_4}$; see Ref. 22 for a discussion of this point; $T = 25^\circ\text{C}$.

Table 4. Second-order rate constants, $k_{\text{obs}}^{\text{sol}}$, for the protonation of anthracene anion radical by phenol and 13 methyl-substituted phenols at $C_{\text{HB}}^{\circ}/C_{\text{A}}^{\circ} = 10$ corrected for the effect of the homoconjugation equilibria (5) and (6). The reaction orders in proton source, defined as $1 + d \log k_{\text{obs}}^{\text{sol}}/d \log C_{\text{HB}}^{\circ}$, are given in parentheses.

Phenol substituent	$k_{\text{obs}}^{\text{sol}}/\text{M}^{-1} \text{ s}^{-1}$			
	DMSO ^a	DMF ^b	PC ^b	MeCN ^b
None	3.40×10^3 (1.01)	6.08×10^3 (1.16)	1.34×10^5 (0.91)	2.81×10^5 (0.99)
2-Methyl	1.54×10^3 (0.95)	3.30×10^3 (1.05)	4.51×10^4 (1.03)	1.29×10^5 (1.00)
3-Methyl	2.46×10^3 (0.95)	3.99×10^3 (1.19)	7.30×10^4 (1.00)	2.21×10^5 (1.09)
4-Methyl	1.45×10^3 (1.04)	2.25×10^3 (1.21)	5.49×10^4 (1.03)	1.27×10^5 (1.19)
2,3-Dimethyl	9.21×10^2 (0.96)	1.74×10^3 (1.12)	2.23×10^4 (1.10)	6.96×10^4 (1.14)
2,4-Dimethyl	7.88×10^2 (0.97)	1.25×10^3 (1.08)	1.57×10^4 (1.20)	5.57×10^4 (1.14)
2,5-Dimethyl	1.31×10^3 (0.93)	1.96×10^3 (1.10)	3.31×10^4 (1.11)	9.12×10^4 (1.12)
2,6-Dimethyl	1.38×10^3 (0.95)	2.36×10^3 (1.06)	1.89×10^4 (1.01)	5.72×10^4 (1.03)
3,4-Dimethyl	1.04×10^3 (1.03)	1.64×10^3 (1.18)	2.40×10^4 (1.31)	9.66×10^4 (1.24)
3,5-Dimethyl	1.66×10^3 (1.01)	3.31×10^3 (1.22)	5.41×10^4 (1.10)	1.47×10^5 (1.18)
2,3,5-Trimethyl	9.46×10^2 (0.94)	1.21×10^3 (1.16)	1.44×10^4 (1.17)	5.19×10^4 (1.16)
2,3,6-Trimethyl	1.13×10^3 (0.90)	1.75×10^3 (1.05)	1.19×10^4 (1.03)	2.70×10^4 (1.04)
2,4,6-Trimethyl	7.29×10^2 (0.91)	1.45×10^3 (1.06)	6.12×10^3 (1.12)	1.49×10^4 (1.04)
3,4,5-Trimethyl	9.90×10^2 (1.04)	1.24×10^3 (1.31)	1.45×10^4 (1.59)	8.56×10^4 (1.27)

^aMechanism (1)–(5), $K_5^{\text{DMSO}} = 2.3 \times 10^3 \text{ M}^{-1}$. ^bMechanism (1)–(4) plus fast and irreversible (5). ^cEquilibrium (6) included with $K_6^{\text{PC}} = K_6^{\text{MeCN}} = 50 \text{ M}^{-1}$. ^dEquilibrium (6) included with $K_6^{\text{PC}} = K_6^{\text{MeCN}} = 70 \text{ M}^{-1}$. ^eEquilibrium (6) included with $K_6^{\text{PC}} = K_6^{\text{MeCN}} = 100 \text{ M}^{-1}$.

as the average of $k_{\text{obs}}^{\text{sol}}$ obtained at the four concentrations $C_{\text{HB}}^{\circ} = 10, 20, 40$ and 80 mM . Comparison of the values of $k_{\text{obs}}^{\text{sol}}$ calculated at $C_{\text{HB}}^{\circ} = 10 \text{ mM}$ (Table 4) with the values of k_2^{sol} given in Table 5 shows that the kinetic contribution from the protonation of $\text{A}^{\cdot-}$ by the hydrogen-bonded dimer, eqn. (11), is typically 10–15 % at $C_{\text{HB}}^{\circ} = 10 \text{ mM}$.

The values of $k_{11}^{\text{sol}} K_7^{\text{sol}}$ obtained as the slopes of the plots are discussed later.

The magnitudes of k_2^{sol} and the effect of methyl substitution.
After correction for the effects of the homoconjugation

equilibria, eqns. (5) and (6), and the kinetic contributions from the dimer, eqn. (11), it is now possible to analyze the effects of methyl substitution in the phenol and the effect of the solvent on k_2^{sol} .

The most striking feature of the data in Table 5 is that the values of k_2^{sol} are one to two orders of magnitude larger for PC and MeCN than for DMSO and DMF. The effect of methyl substitution is qualitatively the same in all four solvents, that is, k_2^{sol} decreases with an increasing number of methyl groups. However, some distinct differences between the solvents become apparent when the $\log k_2^{\text{sol}}$

Table 5. Second-order rate constants, k_2^{sol} , for the protonation of anthracene anion radical by phenol and 13 methyl-substituted phenols corrected for kinetic contributions from HB/HB.^a

Phenol substituent	$k_2^{\text{sol}}/\text{M}^{-1} \text{ s}^{-1}$			
	DMSO	DMF	PC	MeCN
None	$(3.41 \pm 0.05) \times 10^3$	$(5.77 \pm 0.02) \times 10^3$	$(1.26 \pm 0.09) \times 10^5$ ^b	$(2.81 \pm 0.04) \times 10^5$ ^b
2-Methyl	$(1.48 \pm 0.07) \times 10^3$	$(3.50 \pm 0.17) \times 10^3$	$(4.67 \pm 0.19) \times 10^4$	$(1.30 \pm 0.03) \times 10^5$
3-Methyl	$(2.29 \pm 0.11) \times 10^3$	$(3.84 \pm 0.19) \times 10^3$	$(7.37 \pm 0.08) \times 10^4$	$(2.39 \pm 0.16) \times 10^5$
4-Methyl	$(1.51 \pm 0.06) \times 10^3$	$(2.18 \pm 0.16) \times 10^3$	$(5.64 \pm 0.21) \times 10^4$	$(1.25 \pm 0.08) \times 10^5$
2,3-Dimethyl	$(8.84 \pm 0.34) \times 10^2$	$(1.65 \pm 0.05) \times 10^3$	$(2.76 \pm 0.05) \times 10^4$	$(6.84 \pm 0.33) \times 10^4$
2,4-Dimethyl	$(7.59 \pm 0.21) \times 10^2$	$(1.38 \pm 0.10) \times 10^3$	$(1.58 \pm 0.18) \times 10^4$	$(5.70 \pm 0.44) \times 10^4$
2,5-Dimethyl	$(1.22 \pm 0.08) \times 10^3$	$(2.17 \pm 0.21) \times 10^3$	$(3.30 \pm 0.18) \times 10^4$	$(8.98 \pm 0.24) \times 10^4$
2,6-Dimethyl	$(1.30 \pm 0.07) \times 10^3$	$(2.51 \pm 0.14) \times 10^3$	$(1.92 \pm 0.02) \times 10^4$	$(5.96 \pm 0.18) \times 10^4$
3,4-Dimethyl	$(1.05 \pm 0.05) \times 10^3$	$(1.54 \pm 0.01) \times 10^3$	$(2.07 \pm 0.54) \times 10^4$	$(9.53 \pm 0.78) \times 10^4$
3,5-Dimethyl	$(1.67 \pm 0.05) \times 10^3$	$(3.10 \pm 0.06) \times 10^3$	$(5.20 \pm 0.37) \times 10^4$	$(1.50 \pm 0.12) \times 10^5$
2,3,5-Trimethyl	$(9.00 \pm 0.52) \times 10^2$	$(1.18 \pm 0.05) \times 10^3$	$(1.39 \pm 0.04) \times 10^4$ ^b	$(5.19 \pm 0.34) \times 10^4$
2,3,6-Trimethyl	$(1.00 \pm 0.10) \times 10^3$	$(1.95 \pm 0.14) \times 10^3$	$(9.03 \pm 0.24) \times 10^3$	$(2.82 \pm 0.11) \times 10^4$
2,4,6-Trimethyl	$(6.56 \pm 0.55) \times 10^2$	$(1.53 \pm 0.07) \times 10^3$ ^b	$(5.92 \pm 0.05) \times 10^3$	$(1.71 \pm 0.20) \times 10^4$
3,4,5-Trimethyl	$(1.01 \pm 0.36) \times 10^3$ ^b	$(1.03 \pm 0.02) \times 10^3$ ^b	$(9.12 \pm 1.31) \times 10^3$ ^b	$(7.54 \pm 0.41) \times 10^4$ ^b

^aDetermined as the intercept from plots of $k_{\text{obs}}^{\text{sol}}$ vs. C_{HB}° for the reactions with reaction orders ≥ 1.1 (see Table 4). For reaction orders less than 1.1, k_2^{sol} was determined as the average of the four $k_{\text{obs}}^{\text{sol}}$ obtained at $C_{\text{HB}}^{\circ} = 10, 20, 40$ and 80 mM . ^bDetermined from $k_{\text{obs}}^{\text{sol}}$ at $C_{\text{HB}}^{\circ} = 10, 20$ and 40 mM .

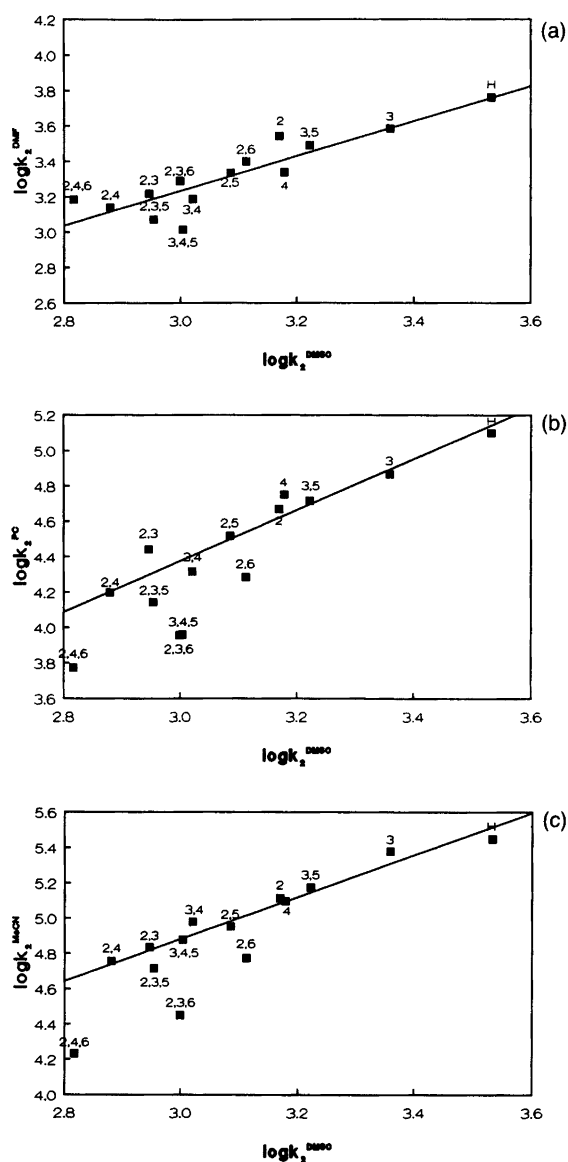


Fig. 1. Plot of the logarithm of the second-order rate constants for protonation of anthracene anion radical by monomeric phenols, k_2^{solv} (Table 5), measured in DMF, PC and MeCN vs. the rate constants measured in DMSO, k_2^{DMSO} . (a) $\log k_2^{\text{DMF}}$ vs. $\log k_2^{\text{DMSO}}$, (b) $\log k_2^{\text{PC}}$ vs. $\log k_2^{\text{DMSO}}$, (c) $\log k_2^{\text{MeCN}}$ vs. $\log k_2^{\text{DMSO}}$. The straight lines represent the regression lines based on (a) all data, (b) all data except those for 3,4,5-trimethylphenol and the 2,6-disubstituted phenols, (c) all data except those for the 2,6-disubstituted phenols.

values are plotted against each other. These plots are shown in Figs. 1(a)–1(c) with DMSO (where kinetic contributions from the dimer could not be detected) chosen as the reference solvent.

It is seen that the plot of $\log k_2^{\text{DMF}}$ vs. $\log k_2^{\text{DMSO}}$ [Fig. 1(a)] exhibits only minor deviations from the regression line ($r = 0.9$). This is in contrast with the plot of $\log k_2^{\text{PC}}$ vs. $\log k_2^{\text{DMSO}}$ [Fig. 1(b)] and in particular of $\log k_2^{\text{MeCN}}$ vs. $\log k_2^{\text{DMSO}}$ [Fig. 1(c)], which show considerable scatter. In both cases the scatter is caused mainly by the data points corresponding to

the 2,6-dimethyl substituted phenols and for the plot of $\log k_2^{\text{PC}}$ vs. $\log k_2^{\text{DMSO}}$ also by the point corresponding to 3,4,5-trimethylphenol. The regression lines shown in Fig. 1(b) and 1(c) were estimated by excluding these data points. Thus, it appears that the protonation of $A^{\cdot-}$ by the 2,6-dimethyl substituted phenols is either 'too slow' in PC and MeCN or 'too fast' in DMSO and DMF, relative to the predictions based on the correlation lines. Moreover, the effect of methyl substitution on the rate constants is *larger* in PC and MeCN than in DMSO and DMF as expressed by the slopes of the regression lines, 1.44 for PC [Fig. 1(b)] and 1.19 for MeCN [Fig. 1(c)]. The origin of the large variation in k_2^{solv} with solvent and the different effects of the methyl groups in the 2,6-positions of the phenol will be discussed in the following.

The solvents, DMSO, DMF, PC and MeCN all have similar relative permittivity, $\epsilon_{\text{DMSO}} = 46.7$, $\epsilon_{\text{DMF}} = 36.7$, $\epsilon_{\text{PC}} = 64.4$ and $\epsilon_{\text{MeCN}} = 37.5^{27}$ and it is seen that the increase in k_2^{solv} on passing from DMSO to MeCN does not parallel the changes in ϵ . In contrast, the change in the magnitude of k_2^{solv} closely parallels the change in the ability of the solvents to act as hydrogen bond acceptors which decrease in the order DMSO > DMF > PC > MeCN as reflected by the values of K_8 given in Table 3 and this suggested to us that the effect of solvent is more likely to be associated with changes in the reactivity of the phenols. For all four solvents the values of K_8 predict the dominant species in solution to be HB/solv, but the data in Table 3 also show that the relative difference between the magnitude of K_8 for the 2,6-dimethyl substituted phenols and all other phenols is relatively larger for DMSO and DMF than for PC and MeCN. In other words, for the 2,6-dimethyl substituted phenols the amount of 'free' phenol is relatively larger in DMSO and DMF which may be the origin of the deviations from the correlation lines observed for these compounds. This is discussed in more detail later.

The reaction mechanism. With HB/solv as the major species, two limiting cases for the detailed mechanism for protonation of $A^{\cdot-}$ may be envisaged. In the first case proton transfer takes place directly from HB/solv in a concerted process in which the hydrogen bond in HB/solv and the phenol O–H bond are broken simultaneously with the formation of the C–H bond. In the second case, proton transfer takes place exclusively from the free HB, and because of the low equilibrium concentration of free HB, this case is a two-step mechanism in which the dissociation of the HB/solv complex takes place prior to the proton transfer. The general question of whether proton transfer from hydrogen bonded acids proceeds via a concerted or a two-step mechanism has been the subject of much discussion, in particular for intramolecularly hydrogen bonded acids, but no generally accepted answer has yet been given, and both mechanisms may account for the observed solvent effect.^{28–31} The discussion is reminiscent of that for nucleophilic substitution reactions in water, where a discrete desolvation step of, for example, amines hydro-

gen bonded to water has been proposed to be involved prior to the nucleophilic attack by the amine.³²

The assumption that the hydrogen atoms of the OH groups in, for example, phenols can participate in only one hydrogen bond at a time and that parallel hydrogen bonding equilibria, as a consequence of this, may be treated as competing individual reactions, resulted in satisfactory data for the effective equilibrium constants for homo- and hetero-conjugation equilibria in different dipolar aprotic solvents.²² Thus, it seems natural to assume that the HB/solv hydrogen bond is essentially broken before bond formation to A⁻ can take place, or in other words, that the limiting two-step mechanism, where only free phenol participates in the proton transfer step is an adequate description of the protonation of A⁻. This view of the mechanism is supported by results obtained in water for the protonation of carbanions which indicated that hydrogen bonds between the acid and water are broken before the actual proton transfer step.^{33,34} Results obtained earlier²⁵ during our studies of protonation of A⁻ using a PhOH/PhO⁻ salt as the proton source, point in the same direction. The experimental data strongly indicated a mechanism in which A⁻ is protonated by PhOH formed by dissociation of the PhOH/PhO⁻ complex with no detectable participation of PhOH/PhO⁻ in the proton transfer step.

The hypothesis of the limiting two-step mechanism with reaction (8) acting as a fast pre-equilibrium permits the evaluation of a set of unique rate constants, k_2 , for the protonation of A⁻ by free HB, because the solvent-dependent equilibrium concentration of free HB can be calculated from the known values of K_8 .

Evaluation of the unique rate constants resulting from the two-step model. The inclusion of the pre-equilibrium step, eqn. (8), results in rate law (16), in which [HB] is the concentration of free phenol. Introduction of an expression for [HB], obtained from eqn. (8), in rate law (16) results in the more convenient form, (17).

$$-\frac{d[A^-]}{dt} = 2k_2[A^-][HB] \quad (16)$$

$$-\frac{d[A^-]}{dt} = 2k_2[A^-] \frac{C_{HB}}{(1 + K_8[\text{solv}])} \quad (17)$$

Here it should be emphasized that what is usually referred to as the rate constant for proton transfer is not k_2 as defined in eqns. (16) and (17), but k_2^{solv} defined in eqns. (2) and (10) and summarized in Table 5.

The rate constants, k_2^{solv} , in Table 5 were calculated from eqn. (10) with the assumption that the concentration of the proton source is equal to C_{HB}^0 corrected for the stoichiometrically determined decrease in concentration of the proton source caused by the formation of homoconjugation complexes and hydrogen bonded dimers. The relation be-

Table 6. Unique second-order rate constants, $k_{2,\text{solv}}$, for proton transfer to anthracene anion radical from free phenols in four dipolar aprotic solvents corrected for the hydrogen bonding between the phenols and the solvents as described in the text.^a

Phenol substituent	$k_{2,\text{solv}}/\text{M}^{-1} \text{ s}^{-1}$				
	DMSO	DMF	PC	MeCN	$\Sigma\sigma$
None	1.0×10^7	5.6×10^6	1.4×10^7	2.8×10^7	0
2-Methyl	2.4×10^6	2.0×10^6	3.4×10^6	9.5×10^6	-0.18 ^b
3-Methyl	5.2×10^6	3.0×10^6	6.8×10^6	2.1×10^7	-0.07
4-Methyl	3.4×10^6	1.7×10^6	5.1×10^6	1.1×10^7	-0.17
2,3-Dimethyl	1.0×10^6	7.3×10^5	1.7×10^6	4.3×10^6	-0.25
2,4-Dimethyl	8.8×10^5	6.0×10^5	9.5×10^5	3.5×10^6	-0.35
2,5-Dimethyl	1.5×10^6	1.0×10^6	2.1×10^6	5.8×10^6	-0.25
2,6-Dimethyl	4.4×10^5	3.8×10^5	5.3×10^5	1.9×10^6	-0.41 ^c
3,4-Dimethyl	1.7×10^6	8.8×10^5	1.5×10^6	6.9×10^6	-0.24
3,5-Dimethyl	3.1×10^6	2.0×10^6	4.2×10^6	1.2×10^7	-0.14
2,3,5-Trimethyl	9.0×10^5	4.6×10^5	7.6×10^5	3.0×10^6	-0.32
2,3,6-Trimethyl	2.7×10^5	2.5×10^5	2.2×10^5	8.2×10^5	-0.48
2,4,6-Trimethyl	1.6×10^5	1.8×10^5	1.3×10^5	4.7×10^5	-0.58
3,4,5-Trimethyl	1.4×10^6	5.3×10^5	6.2×10^5	5.1×10^6	-0.31

^aAt 25°C. ^bEstimated 'best' value, σ_2^b , of σ_2 (see the discussion in the text). ^cEstimated 'best' value, $\sigma_{2,6}^c$, of $\sigma_{2,6}$ (see the discussion in the text).

tween k_2^{solv} and k_2 (or $k_{2,\text{solv}}$ to indicate that k_2 has been obtained from data obtained in the solvent 'solv') is then given by eqn. (18). The application of eqn. (18), together

$$k_{2,\text{solv}} = k_2^{\text{solv}}(1 + K_8[\text{solv}]) \quad (18)$$

with the values of k_2^{solv} from Table 5 and the values of K_8 from Table 3, results in the $k_{2,\text{solv}}$ values summarized in Table 6.

The data for $k_{2,\text{solv}}$ reveal two noteworthy features. First, it is seen that the values of $k_{2,\text{solv}}$ are, in general, two to three orders of magnitude larger than the corresponding values of k_2^{solv} and that the differences between the four solvents are much smaller than those observed for the corresponding four sets of data for k_2^{solv} in Table 5. Secondly, it is seen that the relatively small values of K_8 for the 2,6-dimethyl substituted phenols in DMSO and DMF result only in a moderate increase in k_2 relative to k_2^{solv} when compared with the other phenols. This suggests that the small difference between the rates of proton transfer from the 2,6-dimethyl substituted phenols in DMSO and DMF on the one hand and in PC and MeCN on the other is caused simply by the poor ability of these phenols to form hydrogen bonds even to strong hydrogen bond acceptors such as DMSO and DMF.

The plots of these new data as $\log k_{2,\text{solv}}$ for DMF, PC and MeCN, respectively, against $\log k_2^{\text{solv}}$ for DMSO are shown in Figs. 2(a)–(c). It is evident that the correlations have improved considerably, now resulting in correlation coefficients close to unity, $r = 0.97$ (DMF), $r = 0.97$ (PC) and $r = 0.99$ (MeCN). The plots of the data for DMF and PC [Fig. 2(a) and 2(b)] show that the points corresponding to 2,3,5- and 3,4,5-trimethylphenol deviate most from the

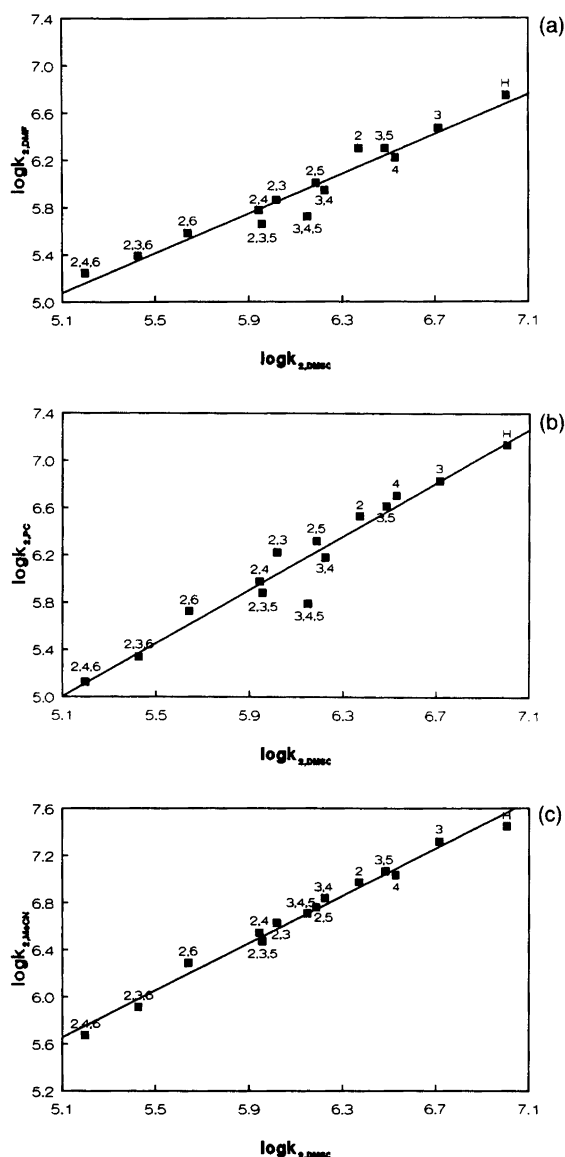


Fig. 2. Correlation of the logarithm of the unique second-order rate constants, $k_{2,\text{solv}}$ (Table 6), calculated from the limiting kinetic model for protonation of anthracene anion radical by phenols in different dipolar aprotic solvents (a) $\log k_{2,\text{DMF}}$ vs. $\log k_{2,\text{DMSO}}$ (slope = 0.84 ± 0.06 , $r = 0.97$), (b) $\log k_{2,\text{PC}}$ vs. $\log k_{2,\text{DMSO}}$ (slope = 1.13 ± 0.08 , $r = 0.97$), (c) $\log k_{2,\text{MeCN}}$ vs. $\log k_{2,\text{DMSO}}$ (slope = 1.00 ± 0.04 , $r = 0.99$).

regression line, but this trend is not observed for the MeCN data [Fig. 2(c)]. It is of interest to note that the large deviations for the 2,6-dimethyl substituted phenols found for the PC and MeCN data in Fig. 1(b) and 1(c) are not apparent when rate constants related to the two-step limiting mechanism are used.

Hammett plots and 'best' values of σ_2 and $\sigma_{2,6}$. In Ref. 22 it was demonstrated that the 'best' Hammett σ values for 2-methyl and 2,6-dimethyl substituted phenols, σ_2^b and $\sigma_{2,6}^b$, depend strongly on the type of reaction used for the definition of σ_2^b and $\sigma_{2,6}^b$. When σ_2^b and $\sigma_{2,6}^b$ were determined from

the hydrogen bonding between the phenols and different hydrogen bond acceptors, $\sigma_2^b = -0.24$ and $\sigma_{2,6}^b = -0.75$ were found as the best values, and once specified, additivity with respect to further substitution was observed. However, values significantly different from these are obtained when σ_2^b and $\sigma_{2,6}^b$ are defined in terms of equilibrium acidity of the phenols. The measured thermodynamic acidity of a phenol in an dipolar aprotic solvent, $\text{p}K^{\text{solv}}$, may be corrected for the hydrogen bonding between the phenol and the solvent to provide the unique thermodynamic acidity of the free phenol, $\text{p}K_{\text{solv}} = \text{p}K^{\text{solv}} - \log(1 + K_8[\text{solv}])$.²² These unique acidities for methyl-substituted phenols in DMSO can then be used to define another set of σ_2^b and $\sigma_{2,6}^b$ for methyl substitution.²² In this case the best values were found to be $\sigma_2^b = -0.08$ and $\sigma_{2,6}^b = -0.24$.

Assuming that the σ values are also additive for the protonation of A^- by methyl-substituted phenols when the proper values of σ_2^b and $\sigma_{2,6}^b$ have been specified, we have estimated the best σ_2^b and $\sigma_{2,6}^b$ values, common for all four solvents, from the k_2 values in Table 6. Because of the small number of phenols unsubstituted in the *ortho* position the σ_2^b and $\sigma_{2,6}^b$ values were determined as the values giving the highest average correlation coefficient for the four correlations. The values obtained by this approach are $\sigma_2^b = -0.18$ and $\sigma_{2,6}^b = -0.41$. The four Hammett plots are shown in Figs. 3(a)–(d), and in all four cases the correlation was found to be respectable with r in the range, 0.978–0.988. The slopes, $\rho(\log k_{2,\text{solv}})$, and the intercepts, which are the interpolated values of $\log k_{2,\text{solv}}$ for PhOH, are given in Table 7.

These values for σ_2^b and $\sigma_{2,6}^b$ based on proton transfer kinetics are in between those determined for the equilibrium constant for hydrogen bond formation and the equilibrium acidity. It is tempting to interpret the magnitude of these reaction-dependent σ_2^b and $\sigma_{2,6}^b$ values as a measure of the tightness of the defining interaction; in the case of the protonation of A^- that is the tightness of the interaction between A^- and the phenol in the transition state. If the O–H bond in the transition state is almost unstretched, the geometry would be expected to be similar to that in a hydrogen bond complex and consequently, the σ^b values would be expected to be close to those found for the hydrogen bonding equilibria. On the other hand, if the O–H bond is almost broken in the transition state, the geometry would be expected to resemble that after complete proton transfer and consequently, the σ^b values would be expected to be close to those determined for the unique acidity. Therefore, the observation that the σ^b values for protonation of A^- by phenols are in between these two limits is in accord with the view that the degree of proton transfer in the transition state is between that for a hydrogen bonded complex and complete proton transfer.

Evaluation of the Brønsted coefficient, α . The general equation for the four Hammett plots in Figs. 3(a)–(d) has the form eqn. (19), where $\rho(\log k_{2,\text{solv}})$ is the ρ value pertaining to this particular Hammett correlation using the σ_2^b and $\sigma_{2,6}^b$

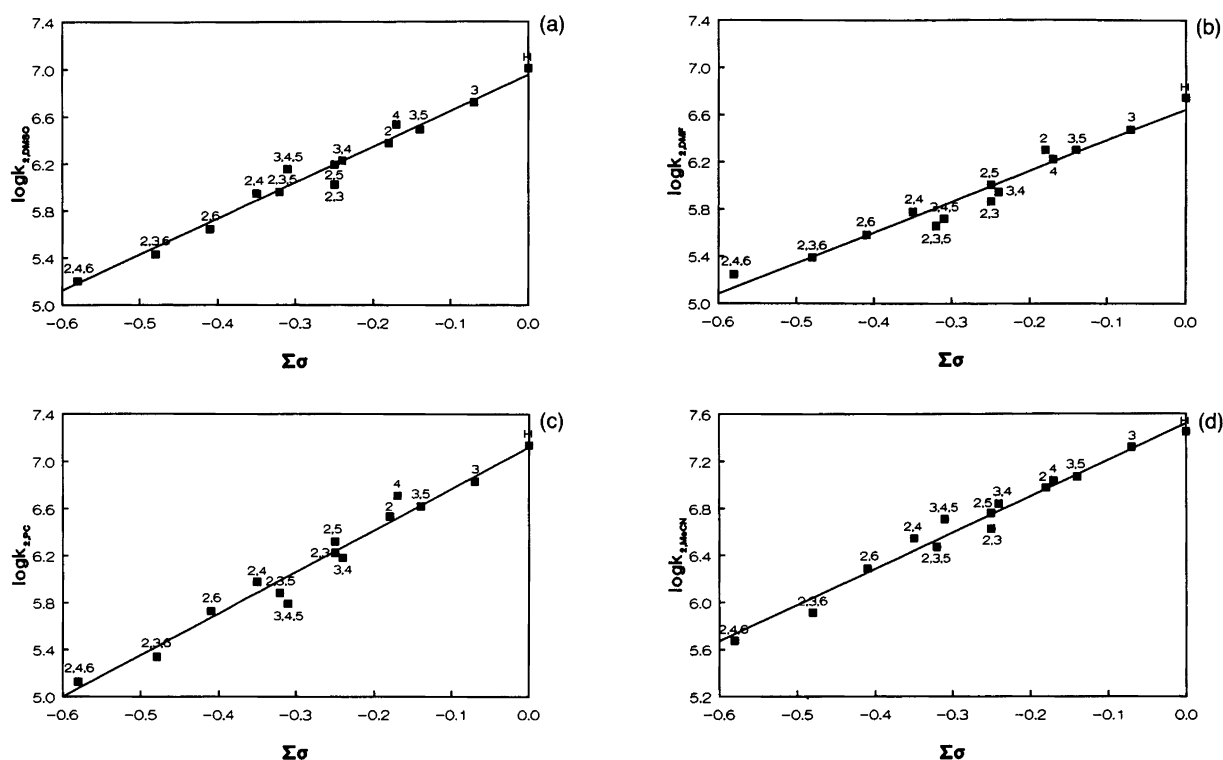


Fig. 3. Hammett plots of the unique second-order rate constants, $k_{2,\text{solv}}$ (Table 6), calculated from the limiting kinetic model for proton transfer from PhOH and 13 methyl-substituted phenols to anthracene anion radical in four dipolar aprotic solvents. The 'best' values, $\sigma_2^b = -0.18$ and $\sigma_{2,6}^b = -0.41$, were chosen as the values for which the maximum average of the four correlation coefficients was obtained. (a) $\log k_{2,\text{DMSO}}$ vs. $\Sigma\sigma$, (b) $\log k_{2,\text{DMF}}$ vs. $\Sigma\sigma$, (c) $\log k_{2,\text{PC}}$, (d) $\log k_{2,\text{MeCN}}$ vs. $\Sigma\sigma$. The slopes, intercepts and correlation coefficients are summarized in Table 7.

values determined above, and $\log k_{2,\text{solv}}(\text{PhOH})$ is the intercept.

$$\log k_{2,\text{solv}} = \rho (\log k_{2,\text{solv}}) \sigma + \log k_{2,\text{solv}}(\text{PhOH}) \quad (19)$$

As mentioned above, the thermodynamic acidities of the free phenols may also be described by a Hammett relation, eqn. (20), where $\text{p}K_{\text{solv}} = \{\text{p}K_{\text{solv}} - \log(1 + K_8[\text{solvent}])\}$ ²² is the unique acidity of the phenol, ρ ($-\text{p}K_{\text{solv}}$) is the ρ value pertaining to the Hammett correlation using $\sigma_2^b = -0.08$ and $\sigma_{2,6}^b = -0.24$ and $-\text{p}K_{\text{solv}}(\text{PhOH})$ is the intercept.

$$-\text{p}K_{\text{solv}} = \rho (-\text{p}K_{\text{solv}}) \sigma - \text{p}K_{\text{solv}}(\text{PhOH}) \quad (20)$$

The two Hammett relations, (19) and (20), can be combined into the Brønsted equation, (21). Owing to the inequality of σ_2^b and $\sigma_{2,6}^b$ in the two Hammett equations, the combination of eqns. (19) and (20) leads, in fact, to three different Brønsted equations, one for the phenols not carrying methyl groups in the *ortho* positions, one for the 2-methyl substituted phenols and one for the 2,6-dimethyl substituted phenols. The three lines have identical slopes but different intercepts [indicated by the constant in eqn. (21)] dependent on the difference between the σ^b values for the unique thermodynamic acidity and for the kinetic data.

Table 7. Slopes, intercepts and regression coefficients for the Hammett plots of the unique rate constants for protonation of anthracene anion radical by free phenols.^a

	DMSO	DMF	PC	MeCN
Slope, $\rho (\log k_{2,\text{solv}})^b$	3.10 ± 0.14	2.65 ± 0.16	3.59 ± 0.19	3.13 ± 0.15
Intercept ^b	6.96 ± 0.08	6.66 ± 0.09	7.13 ± 0.11	7.53 ± 0.08
Regr. coef., r	0.988	0.978	0.983	0.987
$\rho (-\text{p}K_{\text{solv}})^c$	6.53 ± 0.19	5.69 ± 0.27	5.36 ± 0.34	5.08 ± 0.17
α_{solv}^d	0.47 ± 0.03	0.47 ± 0.03	0.67 ± 0.06	0.62 ± 0.04

^aAt $T = 25^\circ\text{C}$. $\sigma_2^b = -0.18$, $\sigma_{2,6}^b = -0.41$. ^bFrom Figs. 3(a)–3(d). ^cFrom Ref. 22. ^d $\alpha_{\text{solv}} = \rho (\log k_{2,\text{solv}}) / \rho (-\text{p}K_{\text{solv}})$.

$$\log k_{2,\text{solv}} = -\{\varrho(\log k_{2,\text{solv}})/\varrho(-\text{p}K_{\text{solv}})\} \text{p}K_{\text{solv}} - \text{p}K_{\text{solv}}/\varrho(-\text{p}K_{\text{solv}}) + \log k_{2,\text{solv}}(\text{PhOH}) + \text{constant} \quad (21)$$

Eqn. (21) shows that the Brønsted α value for the proton transfer reaction between free phenols and anthracene anion radical can be calculated as $\alpha_{\text{solv}} = \varrho(\log k_{2,\text{solv}})/\varrho(-\text{p}K_{\text{solv}})$, that is, the Brønsted α value can be determined as the ratio between the ϱ value defined by the rate constants for the proton transfer reaction, $\varrho(\log k_{2,\text{solv}})$ and the ϱ value defined by the thermodynamic acidity corrected for hydrogen bonding, $\varrho(-\text{p}K_{\text{solv}})$. The values of α_{solv} obtained in this way for the four solvents are also found in Table 7.

Inspection of the α_{solv} values in Table 7 shows a change in α_{solv} from 0.47 in DMSO to 0.67 in PC and the question is whether this may be regarded as a significant difference. Since α was determined as the ratio between two ϱ values, the uncertainty in α results from the uncertainties in both these ϱ values which may be subject to systematic errors not reflected in the statistical standard errors. With respect to the $\varrho(\log k_{2,\text{solv}})$ values, the major systematic uncertainties are associated with the accuracy of the K_8 values and the determination of the σ_2^b and $\sigma_{2,6}^b$ values, where the choice of common values of σ_2^b and $\sigma_{2,6}^b$ in the four solvents is based on the implicit assumption that the degree of interaction between the anion radical and the phenol is the same in all four solvents. The values of σ_2^b and $\sigma_{2,6}^b$ determined for example from the MeCN data alone, which amount to -0.20 and -0.47 , respectively, leads to a $\varrho(\log k_{2,\text{MeCN}})$ value of 2.80, which again results in a value of α_{MeCN} equal to 0.55. This should be compared with the value, 0.63, given in Table 7. With respect to the $\varrho(-\text{p}K_{\text{solv}})$ values, the accuracy of the experimental $\text{p}K_{\text{solv}}$ values varies,²² and for PC in particular where an indirect determination of $\varrho(-\text{p}K_{\text{solv}})$ was used, the accuracy is likely to be much smaller than that indicated by the statistical standard errors. Finally, in the $\text{p}K_{\text{solv}}$ vs. σ correlation it was assumed that the σ_2^b and $\sigma_{2,6}^b$ values determined from the DMSO data were valid for the other three solvents as well, but too few data are available to test this assumption. These uncertainties in the values of $\varrho(\log k_{2,\text{solv}})$ and $\varrho(-\text{p}K_{\text{solv}})$ lead to the conclusion that the errors in α are probably too large to warrant a discussion of the differences observed. We regard the value of α obtained in DMSO (ca. 0.5) the most reliable judged from the quality of the data used in the determination. However, the determination of α for the four solvents is sufficiently accurate to draw the conclusion that α is far from both zero and unity and, in addition, our values are similar to that, 0.6, determined for protonation of a charge-delocalized carbanion, nitrocyclopentadienide, by carboxylic acids in water.³⁵ An α value close to 0.5 may be taken as an indication that the proton is approximately half transferred in the transition state and is thus in accord with the view on the transition state structure based on the values of σ_2^b and $\sigma_{2,6}^b$, determined from the kinetic data.

Analysis of the second-order contribution. On the basis of the limiting two-step mechanism the slopes of the $k_{\text{obs}}^{\text{solv}}$ vs. C_{HB}° plots may now be examined in more detail. Assuming, as before, that only the fraction of the dimer that is not hydrogen bonded to the solvent is active in the protonation of $A^{\cdot-}$, rate law (14) can be reformulated as eqn. (22). Here $[\text{HB}]$ and $[\text{HB}/\text{HB}]$ are the equilibrium concentrations of the free monomer and dimer, respectively, and k_2 and k_{11} are the unique rate constants for protonation of $A^{\cdot-}$ by the free monomer and the free dimer, respectively. Moreover, if it is still assumed that $C_{\text{HB}}^{\circ} = [\text{HB}] + [\text{HB}/\text{solv}]$ we have $[\text{HB}] = C_{\text{HB}}^{\circ}/(1 + K_8[\text{solv}])$. Introduction of this expression for $[\text{HB}]$ in eqn. (22) together with K_7 , the unique equilibrium constant for formation of HB/HB , results in eqn. (23).

$$-\frac{d[A^{\cdot-}]}{dt} = 2[A^{\cdot-}](k_2[\text{HB}] + k_{11}[\text{HB}/\text{HB}]) \quad (22)$$

$$\begin{aligned} -\frac{d[A^{\cdot-}]}{dt} &= 2[A^{\cdot-}]C_{\text{HB}}^{\circ}\{k_2/(1 + K_8[\text{solv}]) \\ &\quad + k_{11}K_7C_{\text{HB}}^{\circ}/(1 + K_8[\text{solv}])^2\} \\ &= 2[A^{\cdot-}]C_{\text{HB}}^{\circ}\{k_2^{\text{solv}} + k_{11}K_7C_{\text{HB}}^{\circ}/(1 + K_8[\text{solv}])^2\} \end{aligned} \quad (23)$$

From eqns. (15) and (23) it is seen that $k_{\text{obs}}^{\text{solv}} = k_2^{\text{solv}} + k_{11}K_7C_{\text{HB}}^{\circ}/(1 + K_8[\text{solv}])^2$, and therefore that the slopes of the plots, $k_{\text{obs}}^{\text{solv}}$ vs. C_{HB}° , are equal to $k_{11}K_7/(1 + K_8[\text{solv}])^2$. By application of the K_8 values from Table 3 and the K_7 values from Ref. 22 together with the slopes obtained from

Table 8. Approximate values of the unique rate constant for protonation of anthracene anion radical by free dimeric phenols.^a

Phenol substituent	$k_{11}/\text{M}^{-1} \text{s}^{-1b}$		
	DMF	PC	MeCN
None	7×10^9	—	—
2-Methyl	—	—	—
3-Methyl	3×10^9	—	—
4-Methyl	2×10^9	—	1×10^9
2,3-Dimethyl	4×10^9	—	4×10^8
2,4-Dimethyl	—	1×10^8	3×10^8
2,5-Dimethyl	—	2×10^8	5×10^8
2,6-Dimethyl	—	—	—
3,4-Dimethyl	7×10^8	7×10^8	9×10^8
3,5-Dimethyl	2×10^9	4×10^8	9×10^8
2,3,5-Trimethyl	3×10^8	6×10^8	2×10^8
2,3,6-Trimethyl	—	—	—
2,4,6-Trimethyl	—	2×10^7	—
3,4,5-Trimethyl	8×10^8	4×10^8	8×10^8

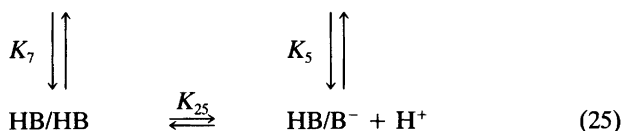
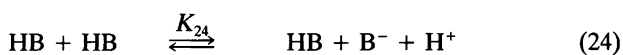
^a Calculated from the slopes of the plots of $k_{\text{obs}}^{\text{solv}}$ vs. C_{HB}° in the cases where the reaction orders ≥ 1.1 . The standard deviations for the slopes are generally in the range 10–50%.
^b $k_{11} = \text{slope} \times (1 + K_8[\text{solv}])^2/K_7$. The values of K_8 are from Table 3 and the values of K_7 are from Ref. 22.

the plots of $k_{\text{obs}}^{\text{soliv}}$ vs. C_{HB}° , the values of k_{11} given in Table 8 were calculated. Only data for the cases where the reaction orders were observed to be larger than 1.1 were used (see above).

Since the slopes of the $k_{\text{obs}}^{\text{soliv}}$ vs. C_{HB}° plots are defined by only four concentrations the uncertainties are fairly large, typically of the order 10–50%, and taking into account the low accuracy of the K_7 values,²² the values of k_{11} can be considered only as estimates. However, very similar values were found in the four cases where k_{11} was determined in the three solvents DMF, PC and MeCN, although k_{11} determined from the data obtained in PC were slightly lower than those determined from the data obtained in DMF and MeCN. The magnitudes of k_{11} are in most cases close to the rate constant for a diffusion-controlled reaction, k_{diff} .³⁶ The values reported are $8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (DMF), $10^9 \text{ M}^{-1} \text{ s}^{-1}$ (PC) and $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ (MeCN), and the lower value of k_{diff} in PC compared with the other two solvents may be one reason for the slightly lower values of k_{11} found in this solvent.

Comparison of the data in Tables 6 and 8 shows that the values of k_{11} are generally two to three orders of magnitude larger than the corresponding values of k_2 and this difference will now be briefly examined in relation to the thermodynamic acidity of the free dimer and the previously determined Brønsted α values.

The relative thermodynamic acidities of free HB and free HB/HB may be estimated from the unique equilibrium constants for dimer formation, K_7 , and homoconjugation, K_5 , by help of the thermodynamic cycle, eqns. (24) and (25) and it is seen that the relative thermodynamic acidity of HB and HB/HB is given by eqn. (26).



$$K_{25}/K_{24} = K_5/K_7 \quad (26)$$

Since the structures of the homoconjugation complexes and the hydrogen bonded dimers are probably very similar, the effect of *ortho* substituents on K_5 and K_7 are expected to be similar too. However, because K_5 is five to six orders of magnitude larger than K_7 it is to be expected that the effect of methyl substitution is, in general, reflected more in K_5 than in K_7 .²² Thus, the decrease in the K_5/K_7 ratio resulting from an increase in the number of methyl substituents is paralleled by a similar decrease of the K_{25}/K_{24} ratio. Introduction of the values of K_5 in Table 2 and the values of K_7 for PhOH (4.7 M^{-1}), 2-methylphenol (2.8 M^{-1}) and 4-methylphenol (4.7 M^{-1})³⁷ in eqn. (26), results in K_{25}/K_{24} equal to 1.4×10^6 , 7.9×10^5 and 1.2×10^6 , respectively. Thus, the dimers, HB/HB, are approximately six pK units more acidic than the corresponding monomers

with the value of K_{26}/K_{25} for 2-methylphenol being approximately a factor of two lower than those for the two other phenols. The magnitude of the decrease upon 2,6-substitution is not known, but if it is considered that K_5 for 2,6-dimethylphenol is approximately one order of magnitude lower than K_5 for unsubstituted phenol (see Table 2) we may put a maximum value of 0.5–1 M^{-1} on K_7 for the 2,6-dimethyl substituted phenols.

With a value of K_{26}/K_{25} of approximately 10^6 and $\alpha \approx 0.5$ as found previously, the relative kinetic acidities of HB/HB and HB, k_{11}/k_2 , is given by $(K_{26}/K_{25})^\alpha$, which is approximately equal to 10^3 for the phenols not methyl-substituted in the 2,6-positions, and somewhat smaller for the 2,6-dimethyl substituted compounds. This leads to estimates of k_{11} in the range 10^8 – $3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ in good agreement with the data in Table 8. However, we should add that the Brønsted α value is probably smaller than 0.5 for a largely diffusion-controlled process, and consequently the estimates of k_{11} should be taken only as an indication that a very fast proton transfer process is indeed expected between HB/HB and A^- .

No significant second-order effects were observed for the most acidic phenols in PC or in MeCN, but the larger experimental uncertainty in the kinetic data for PC and MeCN where the overall reaction is much faster, in particular at high phenol concentrations, leads to a larger uncertainty in the apparent reaction orders. This may well be the origin of the apparent absence of second-order effects under these conditions.

The driving force, ΔG° , for the proton transfer reaction. The driving force, ΔG° , for the proton transfer reaction may be calculated from the value of $\Delta \text{p}K_{\text{DMSO}}$ for the phenol and AH^\cdot . The value of $\text{p}K_{\text{DMSO}}$ for AH^\cdot has been estimated to be 23,³⁸ and, because of its strongly delocalized π -electron system, AH^\cdot is expected to be an extremely weak hydrogen bond donor. Accordingly, we may assume $\text{p}K_{\text{DMSO}} = \text{p}K_{\text{DMSO}}$ for this species. The value of $\text{p}K_{\text{DMSO}}$ for PhOH was found to be equal to 14.5,²² which results in a value of $\Delta \text{p}K_{\text{DMSO}}$ equal to 8.5 corresponding to $\Delta G^\circ = -11.6 \text{ kcal mol}^{-1}$ for the protonation of anthracene anion radical by 'free' PhOH. For the other three solvents similar measurements of $\text{p}K^{\text{soliv}}(\text{AH}^\cdot)$ have not been made, but we may be able to estimate whether a change of solvent from DMSO to either DMF, PC or MeCN is likely to enlarge or diminish the driving force for the proton transfer reaction from the following considerations. When the contribution from the hydrogen bonding between phenol and solvent to the solvation of the phenol is eliminated (by application of $\text{p}K_{\text{soliv}}$ instead of $\text{p}K^{\text{soliv}}$) it may be assumed that the solvent-induced differences in ΔG° for the proton transfer reaction are caused mainly by differences in solvation of the anions, A^- and PhO^- , and that solvation of the neutral species, PhOH and AH^\cdot is of only minor importance. We may further assume that the absolute energy differences between the solvation energies of the phenolate anions are *larger* than the differences between the solvation

energies of the anion radical due to the larger degree of delocalization of the charge in $A^{\cdot-}$ than in PhO^- . From reversible potential measurements in DMSO, DMF and MeCN³⁹ it follows that the difference in solvation of anthracene and anthracene anion radical is smallest in DMSO and approximately equal in DMF and MeCN, while for more charge-localized anion radicals, such as those of nitrobenzenes, the solvation difference varies in the order DMF > MeCN > DMSO. Combined with an overall larger difference between the solvents [$E^\circ(\text{DMSO}) - E^\circ(\text{DMF}) \approx 100$ mV for nitrobenzene, but only ≈ 60 mV for anthracene], this confirms the view that the largest difference between the anion solvating power of the solvents is found for the charge-localized systems.

The acceptor number, AN, defined by Gutmann⁴⁰ is an empirical parameter which is frequently used as a measure of the ability of a solvent to stabilize anions. However, it has been shown⁴¹ that AN may be separated into two solvatochromic parameters, a hydrogen bond donor parameter and a dielectric (polarity/polarisability) parameter, π^* . AN for the four solvents are known⁴⁰ (DMSO: 19.3, DMF: 16.0, PC: 18.0 and MeCN: 19.3), and only MeCN is known to possess weak hydrogen bond donor properties.⁴¹ This means that the order of the solvents changes if only the dielectric contribution, π^* , is considered (DMSO: 1.00, DMF: 0.88 and MeCN: 0.76).⁴¹ The π^* -parameter has not been determined accurately for PC but the polarity effects of PC are comparable to those of DMSO,⁴² and PC, like other esters, apparently does not possess hydrogen bond donor properties.

Thus, to summarize (1) DMF is the poorest anion-solvating solvent, (2) DMSO, PC and MeCN according to the AN have comparable anion-solvating properties, and (3) MeCN, in contrast with the other solvents, stabilizes anions partly via hydrogen bonding. Consequently, we may assume that MeCN only solvates anions as well as DMSO for charge-localized anions for which a well-defined hydrogen bond acceptor site exists. Regarding the two types of anion involved in the proton transfer reaction, $A^{\cdot-}$ and B^- , we may then expect solvation of $A^{\cdot-}$, where the charge is delocalized, to be in the order DMSO > PC > DMF > MeCN based on the π^* values. For the B^- ions, the hydrogen bond acceptor properties will strengthen the solvation by MeCN relative to the other solvents, and the expected order of solvation is DMSO \approx MeCN > PC > DMF based on the values of AN. Consequently, we may expect contributions to ΔG° for the proton transfer reaction from the relative solvation of $A^{\cdot-}$ and B^- to be in the order MeCN > DMSO \geq PC > DMF.

The ordering of the solvents with respect to the contribution to the driving force from differences in solvation of the anion radical and the anion is, except for the PC results which are the most uncertain, qualitatively in agreement with the experimentally observed difference in the rate constants. Furthermore, the solvent-induced differences in the rates are now of the same order of magnitude as the rate differences observed for S_N2 reactions between neutral

substrates and anionic nucleophiles in the same four dipolar aprotic solvents.⁴³

The rather large driving force associated with a k_2 value of $10^7 \text{ M}^{-1} \text{ s}^{-1}$ indicates a large free energy of activation for the protonation of $A^{\cdot-}$. However, this is not special for carbanion radicals. Charge delocalized carbanions generally show the same behavior,^{35,44} and the large energy of activation is normally ascribed to the internal electronic and configurational reorganization in the charge delocalized carbanion necessary in order to localize the charge as required for formation of the hydrogen bonded reactant complex, preceding the actual proton transfer step in aprotic solvents.^{44,45}

Final remarks. The analysis of the kinetic data within the frame of the limiting two-step mechanism allowed for a quantitative treatment of the influence of the specific solvation of the phenols in the dipolar aprotic solvents. The approach was based partly on results available through the literature and partly on results from our own earlier work on protonation of $A^{\cdot-}$ using PhOH/PhO⁻ as the proton source. However, we realize that the limiting mechanism may not be strictly followed in all cases, i.e. that a weak interaction between the phenol and the solvent may still remain at the stage of the reaction where the new C-H bond is being formed. Thus, the second-order rate constants calculated related to the limiting mechanism are maximum values representing the minimum activation energy for protonation of the delocalized anthracene anion radical by the phenols in a dielectric continuum which does not interact specifically with any of the reactants.

The lack of a correlation between k_2^{soln} values for the 2,6-dimethyl substituted phenols found for the four solvents can, within the limiting kinetic model, be explained by the differences in the effects on the strength of hydrogen bonding to the different solvents, and on the effect on the proton transfer step.

Experimental

Reagents, electrodes, cells and instrumentation. Anthracene, phenol, *N,N*-dimethylformamide and dimethyl sulfoxide were obtained as previously described.^{12,25} The preparation procedure for tetrabutylammonium hexafluorophosphate was the same as that previous described for tetrabutylammonium tetrafluoroborate.¹² The solutions of tetrabutylammonium hexafluorophosphate (0.1 M) in dimethyl sulfoxide, *N,N*-dimethylformamide, propylene carbonate (Aldrich, 99 %) or acetonitrile (Merck, spectrograde) were passed through a column filled with neutral alumina (Woelm, W200) immediately before each series of measurements.

In each solvent, samples of 10 ml from the same anthracene solution (1.0 mM) were used for measurements with a number of the phenols, and measurements with unsubstituted phenol were made on all anthracene solutions as an internal standard. The phenol, 2-methylphenol (Fluka),

3-methylphenol (Fluka), 4-methylphenol (Fluka), 2,3-dimethylphenol (Fluka), 2,4-dimethylphenol (Fluka), 2,5-dimethylphenol (Aldrich), 2,6-dimethylphenol (Aldrich), 3,4-dimethylphenol (Aldrich), 3,5-dimethylphenol (Aldrich), 2,3,5-trimethylphenol (Fluka), 2,3,6-trimethylphenol (Ega), 2,4,6-trimethylphenol (Aldrich) and 3,4,5-trimethylphenol (Aldrich) were added from stock solutions (2.5 M) in the actual solvent. Only one set of experiments was carried out for each combination of solvent and proton donor, except for the unsubstituted phenol which, as described above, was used as a standard, and the results are therefore subject to larger random errors than those previously reported.^{13,25} The values of $\nu_{0.5}$ or $\nu_{0.3}$ were, within a single experiment, determined with a precision of $\pm 2\%$. The reproducibility from experiment to experiment (new solvent batch, new stock solutions) was generally to within $\pm 10\%$. The ν_x values for the methyl-substituted phenols relative to ν_x for the unsubstituted phenols are deemed to be precise to within $\pm 5\%$.

The electrodes, cells and instrumentation were as reported earlier,¹² and the cell was thermostatted to $25 \pm 1^\circ\text{C}$ by immersion of the cell in water of that temperature in a closed Dewar flask.

The measurement procedure was the same as previously described,⁴⁶ but for the faster reactions in PC and MeCN the measured parameter was $\nu_{0.3}$ instead of $\nu_{0.5}$. The parameter $\nu_{0.3}$ is the value of the sweep rate corresponding to $R'_i = -I'_i/I'_f = 0.3$, where I'_i and I'_f are the peak values of the derivate cyclic voltammogram on the negative and positive scan, respectively. Consequently, the parameter $\nu_{0.3}$ corresponds to a larger degree of conversion of the anion radical by the proton transfer reaction than $\nu_{0.5}$, and thereby requires the application of smaller sweep rates.

The presence of acidic impurities was tested for by recording of the R'_i value at a sweep rate equal to 1 V s^{-1} before addition of the proton donor. Only in the case of DMSO were small amounts of acidic impurities detected, $R'_i < 1$, but no further purification was carried out. The presence of this acidic impurity is probably the origin of the generally low values of the true reaction order in this solvent.

Digital simulations. The theoretical data used for conversion of the $\nu_{0.5}$ and $\nu_{0.3}$ values to rate constants were obtained by digital simulation. The simulations were carried out in double precision on an HP 9826 A computer. The simulation method was essentially the same as previously described.^{13,19,25}

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NIELSEN AND HAMMERICH

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