

Kinetics of protonation of anthracene radical anions in DMSO by a series of substituted phenols[†]

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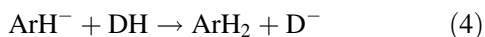
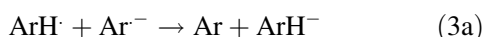
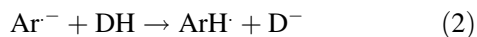
Received 13 December 2002; revised 4 March 2003; accepted 5 March 2003

ABSTRACT: The rate constants k_H for proton transfer from a series of substituted phenols to anthracene radical anions formed in DMSO were measured by the voltammetric method. A quadratic Brønsted dependence of $RT \ln k_H$ against pK_a of phenols was observed. The intrinsic activation barrier ΔG_0^\ddagger calculated on the basis of the known pK_a value for the conjugate acid ArH^+ of the anthracene radical anion is the same as for the reaction in DMF. The homolytic bond dissociation energy (for $ArH^+ \rightarrow Ar + H^+$) was also found to be the same as in DMF. The results obtained are in full agreement with theoretical predictions for protonation of radical anions forming C—H acids, described as the concerted electron and H atom transfer. Copyright © 2003 John Wiley & Sons, Ltd.

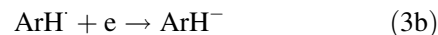
KEYWORDS: protonation kinetics; radical anions; C—H acids

INTRODUCTION

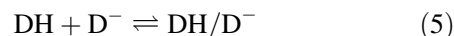
Protonation of aromatic radical anions formed in a variety of organic reactions in electron transfer steps is a fundamental path of their decay because they have much higher Lewis basicity than the parent molecules. The rate constants of that reaction have been intensively studied only for radical anions formed by aromatic hydrocarbons at electrodes in aprotic solvents with the added proton donors and it was shown that the above process occurs according to the disproportionation mechanism DISP1 (also known as the ECE_h mechanism).^{1–9} It involves reversible electron transfer from the electrode, Eqn (1), followed by proton transfer to a radical anion, Eqn (2), which is the rate-determining step (rds), the second electron transfer in solution, Eqn (3a), i.e. the disproportionation reaction, and finally the second proton transfer yielding a dihydro compound, Eqn (4):



However, in the case of phenols with higher acidity, when k_H is sufficiently high, the protonated radical ArH^{\cdot} is formed close to the electrode and the second electron is then transferred, Eqn (3b), from the electrode rather than in solution, Eqn (3a):



leading to the ECE mechanism.^{1,10,11} Moreover, the parallel hydrogen-bonding equilibria, first of all homoconjugation between the proton donor and its anion:



should also be taken into account^{2,3} in order to obtain precise agreement with theoretical predictions under a wide range of experimental conditions. On the other hand, in the aprotic solvents usually used, the formation of dimers $(DH)_2$ can be practically neglected at concentrations of phenol up to 100 mM.⁷ The consequences of the reaction (5) for appropriate treatment of experimental data and the accuracy of the rate constants determined have been examined^{3–5} and a number of rate constants for the protonation of anthracene radical anions in different media by various proton sources have been reported.^{6–9}

However, details of the mechanism of the protonation step itself, Eqn (2), are not well recognized. Recently, it has been proposed by Jaworski¹⁰ that protonation of anthracene radical anions in dimethylformamide (DMF) by substituted phenols can rather be considered as a concerted electron and H atom transfer in a similar way as was originally proposed^{12–14} by the group of Savéant

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[†]Dedicated to Professor T. Marek Krygowski on his 65th birthday.

Contract/grant sponsor: KBN.

Contract/grant number: BST-761/8/2002.

for deprotonation of radical cations including NADH analogues and also polymethylbenzenes and other compounds. The main idea of the Savéant model^{12–14} was a substantial contribution of the homolytic bond dissociation energy D to the intrinsic activation barrier, ΔG_0^\ddagger , i.e. the barrier for the thermodynamic driving force $\Delta G^{o'} = 0$. Our recent comparison of experimental ΔG_0^\ddagger values and estimated D values indicated that protonation in DMF of anthracene radical anions, forming the C—H acid, occurs really as the concerted electron and H atom transfer,¹⁰ whereas for acridine radical anions, forming the 'normal' acid,¹⁵ i.e. N—H acid, the process should be considered as the real proton transfer,¹⁶ with the value of $0.25D$ substantially higher than the experimental ΔG_0^\ddagger value. The results obtained can be explained based on the assumption that during the bond elongation the contribution of covalent states prevails over the contribution of ionic states in a similar manner as was shown¹⁶ for the dissociation of C—H radical cations but not for the conjugate acid of the normal base, pyridine, because this behaviour is much more probable for the acid with a covalent C—H bond than for more ionic N—H and O—H bonds.

In this work, protonation of anthracene radical anions in dimethyl sulphoxide (DMSO) was investigated because thermodynamic and intrinsic contributions to the activation barrier of that process can be determined precisely owing to the known value of equilibrium basicity of anthracene radical anions in DMSO¹⁷ and the detailed mechanism (proton or concerted electron and H atom transfer) was examined.

RESULTS

Protonation rate constants were measured as previously¹⁰ by fitting to the theoretical curve experimental shift of the voltammetric peak potential E_p with the scan rate ν for irreversible electroreduction of anthracene in the presence of phenols. The theoretical curve was obtained^{18,19} neglecting the ohmic drop, assuming the DISP1 mechanism [Eqns (1)–(4)] and pseudo first order for the rds reaction (2) established in solutions of 20–100-fold excess of phenol and described by the unimolecular rate constant k . An example of that fitting for anthracene and three phenols is shown in Fig. 1; E° is the reversible redox potential for the couple hydrocarbon–its radical anion, i.e. for reaction (1) in the absence of any proton donor, F and R are Faraday and gas constants, respectively, and $T = 298$ K is the temperature of measurements. The rate constants k were measured in solutions with five concentrations of each phenol in the range 0.02–0.10 mol dm⁻³. The DISP1 mechanism has been found for the protonation by phenol and substituted phenols in a number of aprotic solvents.^{1,6,7,10} The voltammetric characteristics of the DISP1 and ECE mechanisms are similar¹ and fortunately the k_H values

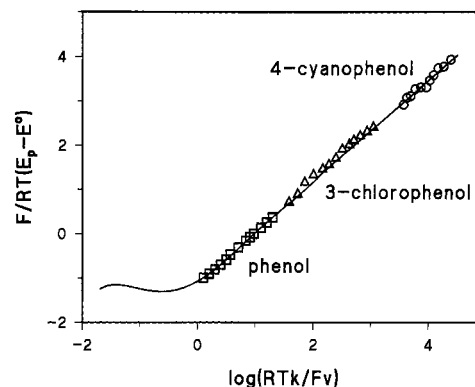


Figure 1. Dependence of the peak potential E_p on the scan rate ν for reduction of 1.0 mmol dm⁻³ anthracene in DMSO in the presence of: 0.02 mol dm⁻³ phenol (\square), 0.08 mol dm⁻³ 3-chlorophenol (\triangle) and 0.10 mol dm⁻³ 4-cyanophenol (\circ)

can be determined in the same manner for both cases. The DISP1–ECE mechanism was supported for each system by the values of a potential shift with the scan rate close to the theoretical value of $\partial E_p / \partial \log \nu = -29.6$ mV per log unit and small deviations predicted recently^{3,5} after taking into account reaction (5) were neglected.

The experimental conditions necessary to determine the rate constants k from voltammetric peak potentials^{4,5,10} according to reactions (1)–(4) were carefully checked: (i) reversibility of the first electron transfer, (ii) purely kinetic control of the process of interest, i.e. fast protonation as compared with the sweep rate $\nu \leq 1$ V s⁻¹, and (iii) pseudo-first-order kinetics at the experimental phenol excess. It has been shown by Nielsen and Hammerich⁵ that the last assumption is fulfilled when the phenol excess is at least 20–40-fold and that deviations from this condition result in lowering of the protonation rate constant, in particular if homoconjugation [Eqn (5)] is taken into account. However, the bimolecular rate constants k_H for protonation of radical anions (calculated from the first-order k values and analytical concentrations of proton sources) for each system do not decrease at the lowest phenol excess but they are independent of the concentration of proton donors within the experimental accuracy. That behaviour is shown in Fig. 2 for the unsubstituted phenol and three phenols with different substituents. The above observation fully supports the assumption of pseudo-first-order kinetics. Moreover, it indicates that the formation of dimers by phenols is not manifested an increase in k_H values at higher phenol concentrations. It can be added that the equilibrium constant for phenol homoconjugation in DMSO^{7,20,21} is equal to 2.3×10^3 mol⁻¹ dm³; unfortunately, the equilibrium constants for the substituted phenols of interest are not known. Neglecting the homoconjugation reaction (5) in data treatment means^{3–5} that the lowering of the phenol concentration at the reaction layer is not taken into account and thus the bimolecular rate constants k_H obtained in this work are underestimated

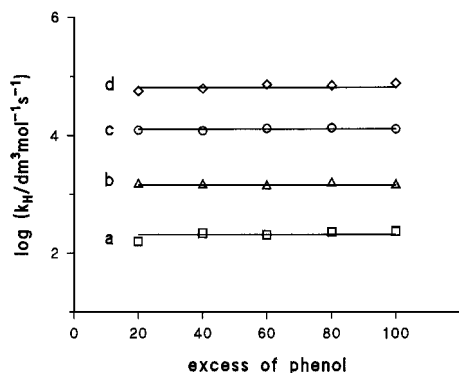


Figure 2. Bimolecular rate constants for protonation of anthracene radical anions in DMSO by (a) 4-hydroxyphenol, (b) phenol, (c) 4-chlorophenol and (d) 2-chlorophenol obtained at different phenol excess (concentration of anthracene = 1.0 mmol dm⁻³)

as in the previous work in DMF.¹⁰ Indeed, the rate constants obtained are slightly lower than those reported by Nielsen and Hammerich^{6,7} for similar conditions but taking into account the effect of homoconjugation: for phenol and 4-methylphenol the values obtained by us are $\log k_H = 3.15$ and 3.0, respectively, whereas the literature values data are $\log k_H = 3.39$ or 3.53 for phenol^{6,7} and 3.18 for 4-methylphenol.⁷ Hence the rate constants determined here, although less accurate, appear reliable for further analysis.

The bimolecular rate constants k_H obtained for protonation of anthracene radical anions in DMSO are given in Table 1. The number of measurements m indicates the total number of voltammograms at different scan rates and phenol concentrations, and the errors of the average k_H values were estimated from Student's distribution with a confidence level of 0.95, taking into account the best fitting of each experimental point.¹⁸ The values of pK_a^{PhOH} for each phenol in DMSO are also given in Table 1; they were obtained in the same laboratory²² and were corrected for the homoconjugation effect,²² and they are also collected in another compilation.²³ The absolute errors of pK_a for phenols²¹ are approximately

Table 1. Rate constants k_H (dm³ mol⁻¹ s⁻¹) for protonation of anthracene radical anions in DMSO at 25 °C by substituted phenols and their acidity

Substituent	pK_a^{PhOH} ^a	m ^b	Log k_H
4-NH ₂	20.75	10	1.81 ± 0.05
4-OH	19.76	13	2.31 ± 0.09
4-CH ₃	18.9	17	3.0 ± 0.1
H	18.00	18	3.15 ± 0.03
4-Cl	16.75	23	4.11 ± 0.04
3-Cl	15.80	26	4.55 ± 0.03
2-Cl	15.00	28	4.82 ± 0.07
4-CN	13.01	55	5.30 ± 0.02
2,4,6-Cl ₃	9.94 ^c	36	6.24 ± 0.07

^a Acidity of phenols in DMSO from Refs 22 and 23.

^b Number of measurements.

^c Estimated in Ref. 10.

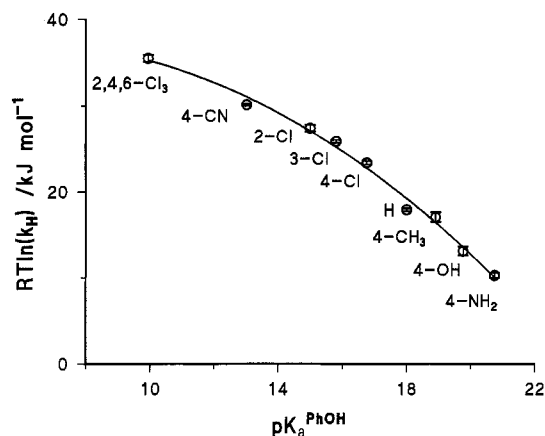


Figure 3. Relationship between bimolecular rate constants k_H for protonation of radical anions of anthracene in DMSO and the acidity of phenols; 95% errors in k_H are indicated

± 0.1. Only the value of pK_a for 2,4,6-trichlorophenol was obtained from the correlation of pK_a in DMSO²² and ACN²⁴ found¹⁰ with a correlation coefficient of 0.9985 for seven phenols.

DISCUSSION

Experimental intrinsic activation barrier

The logarithms of the rate constants obtained depend on pK_a^{PhOH} values and the Brønsted slope for the linear correlation is -0.42 ± 0.07 , indicating that the system is under activation control. However, the experimental points rather fit non-linear relationships as shown in Fig. 3. The quadratic correlation holds with a correlation coefficient $R = 0.996$ and Snedecor test²⁵ $F = 392.3$ and the quadratic term $(pK_a^{\text{PhOH}})^2$ is statistically significant at the level of $\alpha = 0.01$ as calculated using the test²⁵ $F_q = (R^2 - r^2)(n - 3)/(1 - R^2) = 24.32$, where n is the number of experimental points and r is the correlation coefficient of a linear regression $RT \ln k_H$ against pK_a^{PhOH} . Similar curvilinear plots have been observed for other organic reactants,^{26–30} including the protonation of anthracene radical anions by the same phenols in DMF.¹⁰ Such quadratic plots are in agreement with the Marcus theory of proton transfer^{31,32} and also with the theory^{12–14} describing the process of interest as a concerted electron and H atom transfer.

The values of the rate constants in DMSO are very similar to those found previously¹⁰ in DMF, although the pK_a values are higher in DMF. That similarity can be discussed in terms of the thermodynamic driving force in both solvents and the intrinsic activation barrier ΔG_0^\ddagger , which can be calculated according to theoretical models.^{10,12–14,32} For this purpose, the rate constant of bimolecular proton transfer in solution is expressed as

$$RT \ln k_H = RT \ln Z - \Delta G^\ddagger \quad (6)$$

by the difference of the term including collision frequency Z (usually assumed^{10,12–14,26–28,30–32} to be of the order of 10^{11} – 10^{12} mol⁻¹ dm³ s⁻¹) and the Gibbs free energy of activation ΔG^\ddagger . The latter free energy change is described by both theories^{14,31} as a quadratic function of the thermodynamic driving force $\Delta G^{o'}$:

$$\Delta G^\ddagger = w_r + \Delta G_0^\ddagger + 0.5\Delta G^{o'} + (\Delta G^{o'})^2/16\Delta G_0^\ddagger \quad (7)$$

All free energies in Eqn (7) refer to the elementary step at the appropriate separation distance of a reactant pair, have that step is preceded by the formation of a precursor complex, the last process being described in theory by the work term w_r . The reaction free energy change for the activation step $\Delta G^{o'}$ is related to the overall free energy change, given as the difference between the pK_a values for the proton acceptor and donor (e.g. a radical anion and phenol):

$$\Delta G^{o'} = \Delta G^o + w_p - w_r = -2.302RT$$

$$(pK_a^{\text{ArH}} - pK_a^{\text{PhOH}}) + w_p - w_r \quad (8)$$

where w_p is the work required to bring the products together to a mean separation distance³¹ and pK_a^{ArH} is the acidity of neutral radical ArH, the conjugate acid of anthracene radical anion, i.e. K_a^{ArH} is the equilibrium constant for the process



As was discussed in our previous paper,¹⁰ reasonable ΔG_0^\ddagger values can be obtained from the intercept of Eqn (10):

$$\Delta G^\ddagger = \Delta G_0^\ddagger + 0.5\Delta G^o + (\Delta G^o)^2/16\Delta G_0^\ddagger \quad (10)$$

as in the original Marcus treatment,³¹ i.e., only if ΔG^o is known and work terms may be neglected. The last assumption was usually used in the case of a neutral reactant,^{12,14} considering only the electrostatic nature of their interactions. However, in general, work required for the formation of reactants (and products) pair also involves solvation/desolvation phenomena. Nielsen and Hammerich emphasized⁷ that phenol and substituted phenols can form hydrogen bonds with solvents acting as hydrogen bond acceptors, such as DMF or DMSO, and they used the equilibrium constants estimated in CCl₄ for that process (for unsubstituted phenol and DMSO $K = 210$ mol⁻¹ dm³)²⁰ as relative parameters explaining solvent effects on k_H values. As was discussed previously,¹⁰ those constants should be much lower in pure DMSO with much higher electric permittivity. Moreover, the cleavage of a hydrogen bond occurs in the presence of a radical anion and that process cannot be separated from an increase in the O—H bond distance and its polarization and also the simultaneous electrostatic attraction between the radical anion and a positive charge arising at the hydrogen atom. Hence the equilibrium constant

estimated for separate molecules in CCl₄ is too high in the case considered. Excellent Brønsted correlations found in DMSO (Fig. 3) and in DMF¹⁰ additionally support the negligibly small contribution of desolvation of phenols to w_r , because the equilibrium constants for hydrogen bond formation by phenols depend markedly on the substituent²⁰ and do not correlate with pK_a values. Hence it seems reasonable to assume as the first approximation¹⁰ a compensation of different interactions mentioned above and to neglect both work terms in further analysis.

The equilibrium acidity of the protonated anthracene radicals ArH[•] was determined in DMSO ($pK_a^{\text{ArH}} = 23$)¹⁷ using the acidity of 9,10-dihydroanthracene, estimated to be 27. In fact, the last value obtained experimentally by Bordwell *et al.*³³ is equal to 30.1 and from the thermodynamic cycle proposed¹⁷ the acidity of ArH[•] should be equal to 20. The same value was found¹⁰ using the value of acidity in ACN ($pK_a^{\text{ArH}} = 28.4$) obtained³⁴ from the experimental electrochemical potentials and energy change for radical fragmentation measured by photoacoustic calorimetry. The maximum error of pK_a^{ArH} can be up to 5 pK_a units as estimated¹⁰ taking into account the summation of errors [± 2 kcal mol⁻¹ (1 kcal = 4.184 kJ)] for each ΔG^o value in a proper thermodynamic cycle.³⁴

It should be emphasized that the acidity of each phenol and the acidity of anthracene radicals ArH[•] are slightly higher in DMSO than in DMF. Thus, according to Eqn (8), the thermodynamic driving force ΔG^o for protonation by a given phenol in both solvents is similar and, as a consequence, the rate constants in DMSO and DMF are also similar. The above behaviour is evident from the plot of $RT\ln(k_H)$ against ΔG^o shown in Fig. 4 for the results obtained in both solvents. The same quadratic relationship describes all data as shown in the plot. This means that the same intrinsic activation barrier characterizes the process of interest in both solvents.

The intrinsic activation barrier ΔG_0^\ddagger for the reaction in DMSO, which can be found as an intercept ($\Delta G^o = 0$) from regression according to Eqn (10), depends substantially on the value of the collision frequency Z . For

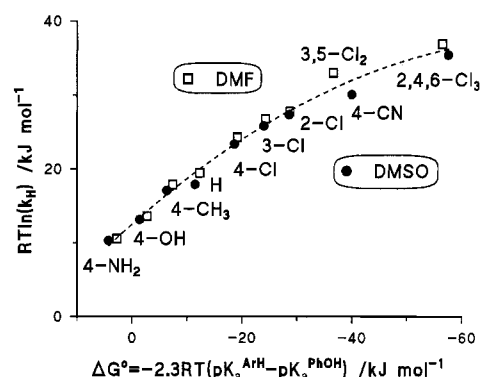


Figure 4. Dependence of the rate constant $RT\ln k_H$ for protonation of anthracene radical anions in DMSO and DMF (from Ref. 10) on the free energy of reaction

deprotonation of radical cations it was assumed^{12–14} that $Z = 3 \times 10^{11} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ (i.e. the mean value calculated from the Smoluchowski equation for homogeneous electron exchange reactions³⁵) but in classical works on proton and hydrogen ion transfer a value of the order of $kT\text{h}^{-1}$ was used.^{26–28,30} Then, for protonation of anthracene radical anion in DMSO, using values of $Z = 3 \times 10^{11}$ and $2 \times 10^{12} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, the intrinsic barrier is equal to $\Delta G_0^\ddagger = 55 \pm 1$ and $59 \pm 1 \text{ kJ mol}^{-1}$, respectively. For the above calculation the k_{H} values were divided by a statistical factor of 2 to take into account the fact^{10,36} that proton may attach to carbon atom in position 9 or 10 in the anthracene radical anion. The 95% errors of ΔG_0^\ddagger values given above are underestimated because the errors in k_{H} and $\text{p}K_{\text{a}}$ values were not taken into account.

The same ΔG_0^\ddagger values can be obtained for this process in DMF ($\Delta G_0^\ddagger = 55 \pm 1$ or $60 \pm 1 \text{ kJ mol}^{-1}$ using the same Z values as above). Bearing in mind that the thermodynamic driving force is practically unaffected by solvent change from DMF to DMSO, the same ΔG_0^\ddagger values found in both solvents explain satisfactorily why the rate constants also do not change substantially.

Homolytic bond dissociation energy

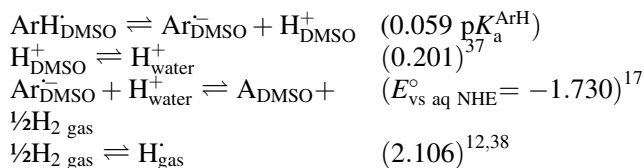
The nature of the intrinsic activation barrier was not explained in the classical Marcus theory^{31,32} but ΔG_0^\ddagger was considered as an additive property and it was thought³² to be the mean of activation barriers for two self-exchange reactions for both acid–base pairs. On the other hand, the last suggestion was justified and two contributions to ΔG_0^\ddagger values were indicated in a theory^{12–14} considering the deprotonation of radical cations as a concerted electron and H atom transfer. However, for the reactants pair of a ‘normal’ base and its conjugate acid the contribution of ionic states prevails over the contribution of covalent states and that self-exchange reaction has a negligibly small activation barrier.¹⁴ On the other hand, this is not the case for the self-exchange reaction of NADH radical cations, where homolytic dissociation (i.e. $\text{ArH}^{\cdot+} \rightarrow \text{Ar}^+ + \text{H}^\cdot$) is energetically preferred¹⁴ and for the neutral radical, the conjugate acid of anthracene radical anion,¹⁰ with the preferred homolytic dissociation $\text{ArH}^\cdot \rightarrow \text{Ar} + \text{H}^\cdot$. Hence only the homolytic bond dissociation enthalpy D of the C—H acid contributes substantially^{10,14,16} to the intrinsic barrier for protonation/deprotonation cross-reactions. Finally, the theory¹⁴ expresses the intrinsic barrier as

$$\Delta G_0^\ddagger = D/4 + \lambda_0/4 \quad (11)$$

where λ_0 is solvent reorganization energy similar to that in the original Marcus theory of electron transfer. It can be added that Eqn (11) has recently been supported experimentally by correlations between ΔG_0^\ddagger and D

with a proper slope.^{12–14} The same theory¹⁴ was successfully applied by one of us¹⁰ to protonation of anthracene radical anion in DMF. For the last process the contribution of homolytic bond dissociation in phenol, a ‘normal’ acid, should be negligibly small but the ΔG_0^\ddagger value was found¹⁰ to be slightly higher than $D/4 = 51 \text{ kJ mol}^{-1}$ for ArH^\cdot radical.

The homolytic bond dissociation enthalpy for the conjugate acid of anthracene radical anion can be estimated¹⁰ from the thermodynamic cycle similar to that proposed by Anne *et al.*¹² The Gibbs free-energy changes for four steps shown in Scheme 1 should be considered and for the resulting process $\Delta G^\circ = 2.307 + 0.059\text{p}K_{\text{a}}^{\text{ArH}} + E^\circ(\text{Ar}/\text{Ar}^{\cdot-})$; the resulting ΔG° and also all contributions given in Scheme 1 are expressed in eV.



Scheme 1

Assuming that entropies of formation of ArH^\cdot and Ar are practically the same and the entropy of formation of $\text{H}_{\text{gas}}^\cdot$ is 27.4 eu,^{12,38} one can obtain (for $\text{p}K_{\text{a}}^{\text{ArH}} = 20$) $D = \Delta G^\circ + T\Delta S^\circ = 2.660 + 0.059\text{p}K_{\text{a}} + E^\circ(\text{Ar}/\text{Ar}^{\cdot-}) = 2.11 \text{ eV}$. Thus, the contribution to the intrinsic barrier is equal to $D/4 = 51 \text{ kJ mol}^{-1}$, which is exactly the same as the value obtained for this process in DMF.¹⁰

The result obtained indicates that the $D/4$ value mainly contributes to the experimental ΔG_0^\ddagger in agreement with theoretical Eqn (11) and supports the conclusion that protonation of anthracene radical anions occurs as the concerted electron and H atom transfer. The difference between ΔG_0^\ddagger and $D/4$, which is the same for the reaction of interest in DMF and DMSO ($4\text{--}8 \text{ kJ mol}^{-1}$), corresponds [Eqn (11)] to the contribution of solvent reorganization energy $\lambda_0/4$. According to the classical Marcus expression the solvent reorganization energy is proportional to the solvent Pekar factor ($\gamma = 1/\varepsilon_{\text{op}} - 1/\varepsilon_{\text{s}}$, where ε_{op} and ε_{s} are optical and static electric permittivity of a solvent, respectively) which is equal to 0.463 and 0.437 for DMF and DMSO, respectively. In full agreement with the results obtained, the difference in $\lambda_0/4$ for both solvents is lower than 1 kJ mol^{-1} , i.e. the error of estimation of ΔG_0^\ddagger .

In conclusion, the results obtained i.e. the quadratic Brønsted dependence, the same intrinsic activation barrier and the same bond dissociation energy in DMF and DMSO, are in full agreement with the theory describing protonation of anthracene radical anions as the concerted electron and hydrogen atom transfer. Finally, it should be added that the concerted process of H atom and electron transfer is not operative for all C—H acids, e.g. it does not work for deprotonation of hydrocarbons, in contrast to deprotonation of their radical cations, when the

oxidation of a parent hydrocarbon molecule results in a decrease in pK_a and the energy of C—H bond dissociation, thus making the above reaction thermodynamically and kinetically favourable.

EXPERIMENTAL

Anthracene (99%) from Aldrich was purified by vacuum sublimation and used at a concentration of 1.0 mmol dm⁻³, and 0.1 mol dm⁻³ tetrabutylammonium perchlorate (Fluka) was used as a supporting electrolyte. 2-Chloro-, 3-chloro-, 4-chloro- and 2,4,6-trichlorophenols (all Pestanal grade, >99.7%, from Riedel-de Haën) were used as received and all other phenols (4-aminophenol, 98%, from Riedel-de Haën, 4-cyanophenol, 98%, from Aldrich, 4-hydroxyphenol from POCh, 4-methylphenol from POCh and unsubstituted phenol, p.a. grade, from Loba Chemie) were purified by vacuum sublimation twice. Five concentrations of phenol (0.02, 0.04, 0.06, 0.08 and 0.10 mol dm⁻³) were normally used. Dimethyl sulphoxide from Sigma-Aldrich (anhydrous, 99.8%) was used as received or was distilled under reduced pressure after drying with neutral alumina.

For voltammetric measurements, a three-electrode cell was used, consisting of a static mercury drop electrode (SMDE) (Laboratorní Přístroje, Prague, Czech Republic), a Pt counter electrode and SCE (or Ag/Ag⁺ in acetonitrile connected by the electrolytic bridge with the Vycor end) as reference electrode. Voltammetric curves at 25 ± 1 °C were recorded with a PAR 273A potentiostat controlled by an IBM PC-386 40 MHz computer by means of the software M270 from PAR. In each solution a number of voltammograms were recorded at different scan rates starting from 0.02 V s⁻¹ and increasing up to the value for which still $\partial E_p/\partial \log v = -29.6$ mV per log unit. Argon gas (Praxair 99.999%) was bubbled through the solution before the experiment and under the solution surface during the measurement.

Acknowledgement

Financial support from KBN by BST-761/8/2002 is gratefully acknowledged.

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