

# Kinetics of protonation of anthracene and phenanthrene radical anions in DMF by a series of substituted phenols. Comparison of Brønsted and Hammett plots



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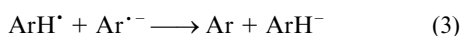
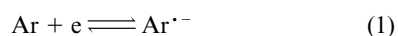
Received (in Cambridge, UK) 21st June 1999, Accepted 6th October 1999

The rate constants  $k_{\text{H}}$  for the proton transfer from a series of substituted phenols to anthracene and phenanthrene radical anions formed in DMF have been measured by the voltammetric method. The quadratic Brønsted dependencies of  $RT \ln k_{\text{H}}$  against  $\text{p}K_{\text{a}}$  of phenols for both radical anions were observed. For the conjugate acid  $\text{ArH}^{\bullet}$  of the anthracene radical anion  $\text{p}K_{\text{a}}$  is known and the intrinsic activation barrier  $\Delta G_{\text{o}}^{\ddagger} = 59 \text{ kJ mol}^{-1}$  was calculated. The homolytic bond dissociation energy  $D$  for  $\text{ArH}^{\bullet} \rightarrow \text{Ar} + \text{H}^{\bullet}$  was evaluated and the obtained value of  $D/4 = 51 \text{ kJ mol}^{-1}$  is in good agreement with the theoretical prediction  $\Delta G_{\text{o}}^{\ddagger} = (D + \lambda_{\text{o}})/4$  (where  $\lambda_{\text{o}}$  is the solvent reorganization energy) based on a recent theory of the deprotonation of radical cations described as a concerted electron and H atom transfer. However, linear Hammett plots of  $\log k_{\text{H}}$  against  $\sigma$  were observed for both radical anions and the lack of a quadratic effect was explained as a result of a through-resonance contribution. On the other hand, the application of normalized substituent constants  $\sigma^{\circ}$  resulted in the quadratic Hammett plots in accordance with the Reactivity Selectivity Principle.

## Introduction

Aromatic radical anions formed by electron transfer steps in a variety of organic reactions have much higher Lewis basicity than their parent molecules and thus the protonation of those intermediates is a fundamental step in their decay. The equilibrium basicity of radical anions has not been determined in non-aqueous solvents with the exception of anthracene radical anion in dimethyl sulfoxide (DMSO)<sup>1</sup> and acetonitrile (ACN).<sup>2</sup> However the less characteristic parameter—acidity—is available for a number of radical anions;<sup>3</sup> all these parameters have been obtained using thermodynamic cycles.

The rate constant for the protonation of radical anions, in particular those formed by aromatic hydrocarbons at electrodes in aprotic solvents with added proton donors, can be easily determined. In dimethylformamide (DMF) for slower rates ( $10^{-1}$ – $10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) with water as a proton donor, spectroscopic methods have been used;<sup>4</sup> for higher rates ( $10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) with phenol as the source of protons, double-potential-step chronoamperometry and voltammetric methods have been applied.<sup>5–7</sup> In some earlier studies it was shown that the electrochemical reduction of aromatic hydrocarbons in DMF in the presence of proton donors occurs according to the disproportionation mechanism DISP1<sup>8</sup> (also known as an ECE<sub>h</sub> mechanism) shown in eqns. (1)–(4). This involves revers-



ible electron transfer from the electrode (1) followed by proton transfer to a radical anion (2), which is the rate determining step (rds), then a second electron transfer in solution (3), *i.e.* the disproportionation reaction, and finally a second proton transfer yielding the dihydrocompound (4).

Some inconsistencies in the experimental results were found after further extensive work.<sup>9</sup> These were finally explained in an elegant contribution,<sup>10</sup> proposing that parallel hydrogen-bonding equilibria (first of all the homoconjugation between the proton donor and its anion, eqn. (5), and then the form-

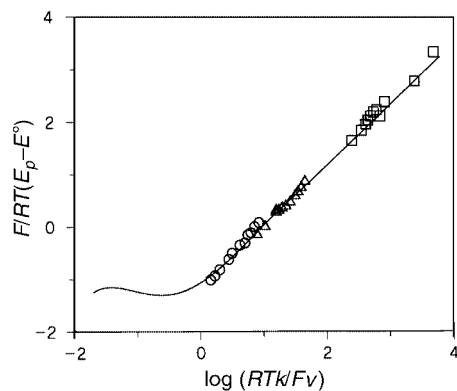


ation of dimers, eqn. (6)) should also be taken into account in



order to obtain precise agreement with the theoretical predictions. In particular, reaction (5) which can be treated in the limiting mechanism as a fast and irreversible step,<sup>10–13</sup> results in a change of the overall reaction stoichiometry from two to four molecules of proton donor consumed per two molecules of  $\text{Ar}^{\bullet -}$ . The consequences of reactions (5) and (6) to the proper treatment of experimental data and the accuracy of the rate constants determined have been examined<sup>10–12</sup> and a number of rate constants for the protonation of anthracene radical anions in different media by various proton sources have been reported recently.<sup>13–15</sup>

In this paper the rate constants for the protonation of anthracene and phenanthrene radical anions are measured, using as proton donors a series of substituted phenols with a wide range of acidity,  $\text{p}K_{\text{a}}^{\text{PhOH}}$ . Our aim was to separate the thermodynamic and kinetic contributions to the observed rate constants according to the Marcus theory<sup>16</sup> and a model recently proposed<sup>17–19</sup> for the deprotonation of cation radicals, as well as to compare linear *versus* quadratic effects in Brønsted and Hammett plots. The last question has been repeatedly addressed in the literature.<sup>20–22</sup> In particular, Pross has argued<sup>20</sup> on the basis of the Reactivity Selectivity Principle (which states that more reactive species tend to be less selective in their reactivity) that there is a contradiction between the observed non-linear behaviour of the Brønsted relation (supported by theoretical models<sup>16–19</sup>) and the overwhelming evidence for linear Hammett plots. Additional explanations

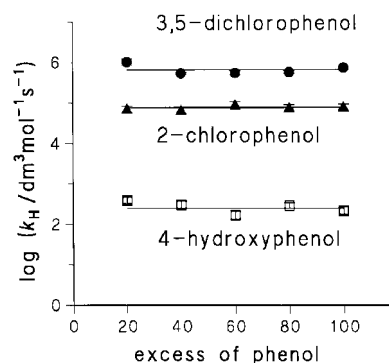


**Fig. 1** Dependence of the peak potential  $E_p$  on the scan rate  $\nu$  for the reduction of  $0.5 \text{ mmol dm}^{-3}$  anthracene in DMF in the presence of:  $0.02 \text{ mol dm}^{-3}$  3,5-dichlorophenol ( $\square$ ),  $0.04 \text{ mol dm}^{-3}$  4-chlorophenol ( $\triangle$ ) and  $0.05 \text{ mol dm}^{-3}$  4-hydroxyphenol ( $\circ$ ).

were based<sup>21</sup> on a more general intersecting-state model. The experimental data presented in this paper demonstrate another aspect of that problem.

## Results

The protonation rate constant was measured by fitting to the theoretical curve the experimental shift of the voltammetric peak potential  $E_p$  with the scan rate  $\nu$  for the irreversible electroreduction of anthracene and phenanthrene in the presence of phenols. A theoretical curve was obtained<sup>23,24</sup> neglecting the ohmic drop, assuming the DISP1 mechanism (1)–(4) and the pseudo first-order of the rds reaction (2), established in solutions of 20 to 100-fold excess of phenol and described by the unimolecular rate constant  $k$ . An example of that fitting for the anthracene and three phenols is shown in Fig. 1;  $E^0$  is the reversible redox potential for the couple: hydrocarbon/its radical anion, *i.e.* for the reaction (1) in the absence of any proton donor;  $F$  and  $R$  are Faraday and gas constants, respectively;  $T = 297 \text{ K}$  is the temperature of measurements. The rate constants  $k$  were measured in solutions with five concentrations of each phenol in the range  $0.01$ – $0.05 \text{ mol dm}^{-3}$ ; for anthracene radical anion higher concentrations of unsubstituted phenol up to  $0.1 \text{ mol dm}^{-3}$  were also examined. For 2,4,6-trichlorophenol the upper concentration limit was  $0.03 \text{ mol dm}^{-3}$  for anthracene; for phenanthrene it was impossible to use that proton donor because of a change in the voltammogram shape, indicating a more complex mechanism, which was not examined in detail. The assumed DISP1 mechanism was supported by a comparison with the literature data as well as by experimental evidence. The DISP1 mechanism (originally called<sup>4</sup> the regeneration mechanism) was established in DMF for the protonation of radical anions of aromatic hydrocarbons by water. A linear dependence with the correlation coefficient of 0.9999 is observed between  $\log k_H$  values for the protonation in DMF of radical anions of anthracene, phenanthrene and naphthalene by water<sup>4</sup> and  $\log k_H$  found in this work ( $k_H = 1.0 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for naphthalene radical anion) with the use of *p*-chlorophenol as a proton donor, indicating the same mechanism. However, in the case of phenols with higher acidity, when  $k_H$  is sufficiently high, the protonated radical  $\text{ArH}^{\cdot}$  is formed close to the electrode and the second electron is then transferred from the electrode rather than in solution (3), leading to the ECE mechanism.<sup>7,8</sup> The voltammetric characteristics for DISP1 and ECE mechanisms are similar<sup>8</sup> and fortunately the upper part of the theoretical curve (Fig. 1) does not change, so the  $k_H$  values 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  $\partial E_p / \partial \log \nu = -29 \text{ mV/log unit}$



**Fig. 2** Bimolecular rate constants for the protonation of anthracene radical anions in DMF by 3,5-dichlorophenol, 2-chlorophenol and 4-hydroxyphenol obtained at different phenol excess (the concentration of anthracene is equal to  $0.5 \text{ mmol dm}^{-3}$ ).

and small deviations predicted recently<sup>10,12</sup> after taking into account reactions (5) and (6), were neglected.

The experimental conditions necessary for the determination of the rate constants  $k$  from the voltammetric peak potentials<sup>11–12</sup> according to reactions (1)–(4) were carefully checked: (i) the first electron transfer (1) is reversible and does not participate in the rate control at sweep rates used, (ii) the reaction is under purely kinetic control, *i.e.*, the protonation is fast as compared with the sweep rate  $\nu \leq 1 \text{ V s}^{-1}$  (a dimensionless parameter  $kRT/\nu nF > 0.83$ ) and (iii) the process of interest can be treated by pseudo first-order kinetics at the experimental 20 to 100-fold phenol excess. It was recently shown by Nielsen and Hammerich<sup>12</sup> that the last assumption is fulfilled when the phenol excess is at least 20 to 40-fold and that deviations from this condition result in a lowering of the protonation rate constant, in particular if homoconjugation (5) is taken into account. However, the bimolecular rate constants,  $k_H$ , for the 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 phenol concentration within experimental accuracy. That behaviour is shown in Fig. 2 for the anthracene radical anion and three phenols with different substituents. The above observation fully supports the assumption of pseudo first-order kinetics as well as indicating that the reaction (6) is not manifested by the increase of  $k_H$  values at higher phenol concentrations. It can be added that the estimated equilibrium constants of reaction (6) for unsubstituted phenol in aprotic solvents<sup>14,25</sup> is very low (of the order of  $5 \text{ mol}^{-1} \text{ dm}^3$ ), *i.e.*, it is much lower than the equilibrium constant found for the phenol homoconjugation in DMF ( $7 \times 10^3 \text{ mol}^{-1} \text{ dm}^3$ ).<sup>14</sup> Unfortunately, the equilibrium constants for the substituted phenols of interest are not known. Neglecting the homoconjugation reaction (5) in data treatment means that a lowering of the phenol concentration at the reaction layer<sup>10–12</sup> is not taken into account and thus, the bimolecular rate constants  $k_H$  obtained in this work are underestimated. However, they are close to recent literature values: for phenol, 4-methylphenol and 4-chlorophenol the obtained values are equal to  $\log k_H = 3.42$ , 3.14 and 4.27, respectively, and Nielsen and Hammerich, taking into account the full reaction scheme (1)–(6), reported<sup>12,14</sup>  $\log k_H = 3.761$ , 3.33 and 4.70, respectively. Thus, the rate constants determined, although less accurate, look reliable for the further analysis of Brønsted and Hammett plots.

The bimolecular rate constants  $k_H$  obtained for the protonation of anthracene and phenanthrene radical anions in DMF are collected 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.<sup>23</sup> The values of  $\text{p}K_a^{\text{PhOH}}$  for each phenol

**Table 1** The rate constants  $k_{\text{H}}$  ( $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ ) for the protonation of anthracene and phenanthrene radical anions in DMF at 24 °C by substituted phenols, their acidity and substituent constants

| Substituent           | $\sigma^a$        | $\text{p}K_{\text{a}}^{\text{PhOH}}$ | Anthracene |                     | Phenanthrene |                     |
|-----------------------|-------------------|--------------------------------------|------------|---------------------|--------------|---------------------|
|                       |                   |                                      | $m^c$      | $\log k_{\text{H}}$ | $m^c$        | $\log k_{\text{H}}$ |
| 4-NH <sub>2</sub>     | -0.66 (-0.36)     | 21.48                                | 45         | 1.85 ± 0.07         | 31           | 2.68 ± 0.02         |
| 4-OH                  | -0.37 (-0.16)     | 20.53                                | 78         | 2.39 ± 0.04         | 52           | 3.32 ± 0.03         |
| 4-CH <sub>3</sub>     | -0.17 (-0.12)     | 19.7                                 | 72         | 3.14 ± 0.03         | 32           | 3.75 ± 0.06         |
| H                     | 0                 | 18.84                                | 30         | 3.42 ± 0.05         | 26           | 4.19 ± 0.07         |
| 4-Cl                  | 0.23              | 17.64                                | 77         | 4.27 ± 0.02         | 70           | 5.22 ± 0.04         |
| 3-Cl                  | 0.37              | 16.73                                | 73         | 4.72 ± 0.03         | 19           | 5.42 ± 0.09         |
| 2-Cl                  | —                 | 15.96                                | 92         | 4.89 ± 0.02         | 41           | 6.00 ± 0.06         |
| 3,5-Cl <sub>2</sub>   | 0.74 <sup>b</sup> | 14.58                                | 66         | 5.82 ± 0.04         | 40           | 6.36 ± 0.08         |
| 2,4,6-Cl <sub>3</sub> | —                 | 11.1                                 | 38         | 6.5 ± 0.1           | —            | —                   |

<sup>a</sup> Substituent constants  $\sigma_m$  and  $\sigma_p$  from ref. 30; normalized substituent constants for electron-releasing *para*-substituents extracted from ref. 31 are given in parentheses. <sup>b</sup> Additivity of  $\sigma_m$  was assumed. <sup>c</sup> Number of measurements.

in DMF are also given in Table 1; they were calculated using eqn. (7) proposed by Maran *et al.*<sup>26</sup> which provides the acidities

$$\text{p}K_{\text{a}}^{\text{DMF}} = 1.56 + 0.96 \text{p}K_{\text{a}}^{\text{DMSO}} \quad (7)$$

in DMF with a standard deviation of 0.4  $\text{p}K_{\text{a}}$  units from the data in DMSO.

All  $\text{p}K_{\text{a}}^{\text{DMSO}}$  values were obtained in the same laboratory<sup>27</sup> and were corrected for the homoconjugation effect.<sup>27</sup> This procedure looks more precise than the use of  $\text{p}K_{\text{a}}$  values measured directly in DMF in different laboratories with different standards, as can be seen from the inspection of a recent compilation.<sup>28</sup> Only the value of  $\text{p}K_{\text{a}}$  for 2,4,6-trichlorophenol was obtained from the correlation (8) of  $\text{p}K_{\text{a}}$  in DMSO<sup>27</sup> and

$$\text{p}K_{\text{a}}^{\text{ACN}} = 12.4 + 0.80 \text{p}K_{\text{a}}^{\text{DMSO}} \quad (8)$$

ACN,<sup>29</sup> found with the correlation coefficient of 0.9985 for 7 phenols [with substituents: 3,5-Me<sub>2</sub>; H; 3-NO<sub>2</sub>; 3,5-Cl<sub>2</sub>; 4-NO<sub>2</sub>; 2,4-(NO<sub>2</sub>)<sub>2</sub> and 2,6-(NO<sub>2</sub>)<sub>2</sub>].

## Discussion

### Brønsted plots and the intrinsic barrier

For both anion radicals the logarithms of the rate constants obtained depend on  $\text{p}K_{\text{a}}^{\text{PhOH}}$  values, and Brønsted slopes (or symmetry factors) for linear correlations are equal to  $-0.56 \pm 0.04$  and  $-0.47 \pm 0.04$  for phenanthrene and anthracene radical anions, respectively, indicating that both systems are under activation control. However, experimental points rather fit non-linear relationships as shown in Fig. 3. The quadratic correlation (9) holds with the correlation coefficients of  $R = 0.997$ ,

$$RT \ln k_{\text{H}} = a + b \text{p}K_{\text{a}}^{\text{PhOH}} + c (\text{p}K_{\text{a}}^{\text{PhOH}})^2 \quad (9)$$

the Snedecor test<sup>32</sup>  $F = 536.0$  for anthracene and  $R = 0.995$ ,  $F = 269.7$  for phenanthrene radical anions. The quadratic term  $(\text{p}K_{\text{a}}^{\text{PhOH}})^2$  is statistically significant at the level of  $\alpha = 0.01$  and  $\alpha = 0.10$  for the anthracene and phenanthrene systems, respectively, as calculated using the test<sup>32</sup>  $F_q = (R^2 - r^2)(n - 3)/(1 - R^2)$  where  $n$  is the number of experimental points and  $r$  is the correlation coefficient of a linear regression  $RT \ln k_{\text{H}}$  against  $\text{p}K_{\text{a}}^{\text{PhOH}}$ ;  $F_q = 40.13$  and  $4.67$  for the anthracene and phenanthrene radical anions, respectively. Similar curvilinear plots were observed for other organic reactants<sup>33-37</sup> including deprotonation of aromatic radical cations<sup>17-19,38</sup> and were used to obtain the intrinsic activation barrier.

For that purpose quadratic Brønsted relationships were considered in terms of the Marcus theory of proton transfer<sup>16,39</sup> as well as the recent theory<sup>17-19</sup> of the deprotonation of radical cations, originally NADH analogues but also polymethyl-

benzenes<sup>38</sup> and other radical cations from the literature data. In that new model it was argued<sup>17-19</sup> that deprotonation of radical cations should be rather described as a concerted electron and H atom transfer and thus, the theory of the dissociative electron transfer<sup>40</sup> is applicable to dynamics of the process under consideration. That new model<sup>17-19</sup> can better justify an extension of the Marcus theory (originally developed for outer-sphere electron transfer) to the proton transfer and moreover it can explain the nature of the intrinsic barrier. Before further discussion let us note that the rate constant for the bimolecular proton transfer in solution, given by eqn. (10), includes the

$$RT \ln k_{\text{H}} = RT \ln Z - \Delta G^\ddagger \quad (10)$$

collision frequency (normally assumed<sup>16-19,38,39</sup> to be  $Z \approx 10^{11} \text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$ ) and the Gibbs free energy of activation  $\Delta G^\ddagger$  described by both theories<sup>16,19</sup> as a quadratic function of the thermodynamic driving force  $\Delta G^{o'}$ , [eqn. (11)], where  $\Delta G_o^\ddagger$  is

$$\Delta G^\ddagger = w_r + \Delta G_o^\ddagger + 0.5 \Delta G^{o'} + (\Delta G^{o'})^2 / 16 \Delta G_o^\ddagger \quad (11)$$

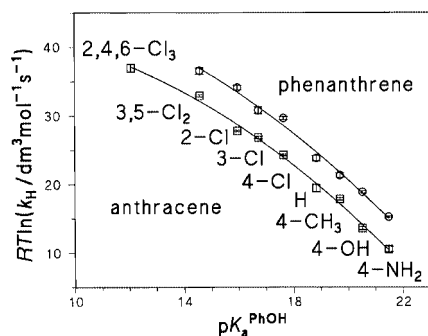
the intrinsic activation barrier, *i.e.*  $\Delta G^\ddagger$  for  $\Delta G^{o'} = 0$ . All free energies in eqn. (11) refer to the elementary step at the proper separation distance of the reactant pair and thus that step is preceded by the formation of the precursor complex; the last process is described 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 a difference between the  $\text{p}K_{\text{a}}$  values for the proton acceptor and donor (*e.g.* a radical anion and phenol), [eqn. (12)], where  $w_p$  is the work required to bring

$$\Delta G^{o'} = \Delta G^o + w_p - w_r = -2.302RT(\text{p}K_{\text{a}}^{\text{ArH}} - \text{p}K_{\text{a}}^{\text{PhOH}}) + w_p - w_r \quad (12)$$

the products together to a mean separation distance<sup>16</sup> and  $\text{p}K_{\text{a}}^{\text{ArH}}$  is the acidity of the conjugate acid of the anthracene radical anion, *i.e.*  $K_{\text{a}}^{\text{ArH}}$  is the equilibrium constant for process (13).



In a number of papers when the  $\text{p}K_{\text{a}}$  of one reactant was not known the intrinsic activation barrier  $\Delta G_o^\ddagger$  was obtained<sup>33,34,36,38</sup> from the coefficient  $c$  at the quadratic term in the Brønsted equation (9) and a further analysis of the coefficient  $a$  resulted in an estimation of the  $w_r$  term. However, it was recently suggested<sup>17</sup> that the precision of experimental data does not allow for that procedure. Instead of that, in the case of reactions between radical cations and neutral bases, Anne *et al.*<sup>17-19</sup> neglected the work terms and obtained  $\Delta G_o^\ddagger$  values from the intercept of eqn. (14), as in the original Marcus treatment.<sup>39</sup>



**Fig. 3** Relationships between bimolecular rate constants  $k_H$  for the protonation of radical anions of anthracene ( $\square$ ) and phenanthrene ( $\circ$ ) and the acidity of phenols; the 95% errors in  $k_H$  are indicated.

The procedure,<sup>33,36,38</sup> based on the use of the coefficient at the quadratic term in eqns. (9), (11) or (14), is indeed incorrect and

$$\Delta G^\ddagger = \Delta G_o^\ddagger + 0.5\Delta G^\circ + (\Delta G^\circ)^2/16\Delta G_o^\ddagger \quad (14)$$

gave  $\Delta G_o^\ddagger$  values too small but the origin of that behaviour was not recognized. The fitting of experimental data to a quadratic equation by the least squares method gives only the intercept correct because both parameters  $\Delta G^\circ$  and  $(\Delta G^\circ)^2$  (or  $pK_a$  and  $(pK_a)^2$  in eqn. (9)) are statistically not independent. On the other hand, fitting experimental data to  $\Delta G^\ddagger - 0.5\Delta G^\circ = \Delta G_o^\ddagger + (\Delta G^\circ)^2/16\Delta G_o^\ddagger$  is statistically correct, however, only the intercept is obtained with a acceptable accuracy. It means that reasonable  $\Delta G_o^\ddagger$  values can be obtained only if  $\Delta G^\circ$  is known and work terms may be neglected.

Considering only the electrostatic interactions between ions the values of  $w_r$  and  $w_p$  were usually neglected in the case of one neutral reactant.<sup>17,19</sup> However in general, works required for the formation of reactants (and products) pair have a complex nature and involve electrostatic interactions as well as solvation/desolvation phenomena. Nielsen and Hammerich have recently emphasized<sup>14</sup> that phenol and substituted phenols can form hydrogen bonds with solvents acting as hydrogen bond acceptors, like DMF, and they used the equilibrium constants estimated in  $CCl_4$  for that process (for unsubstituted phenol and DMF  $K = 75 \text{ mol}^{-1} \text{ dm}^3$ )<sup>25</sup> as relative parameters explaining solvent effects on  $k_H$  values. As a matter of fact a lower equilibrium constant can be expected in DMF on the basis of its higher electric permittivity. Moreover, the breaking of a hydrogen bond occurs in the presence of a radical anion and that process cannot be separated from an increase of the O–H bond distance and its polarization, as well as some simultaneous electrostatic attraction between a radical anion and a positive charge arising then at a hydrogen atom. Thus, the equilibrium constant estimated for separated molecules in  $CCl_4$  is too high in the considered case. The excellent Brønsted correlations found (Fig. 3) additionally support a negligibly small contribution from the desolvation of phenols to  $w_r$ , because the equilibrium constants for hydrogen bond formation by phenols depend markedly on a substituent<sup>25</sup> and do not correlate with  $pK_a$  values. Thus, it looks reasonable to assume in the first approximation a compensation of different interactions mentioned above and to neglect the both work terms in the further analysis.

Unfortunately, values of  $\Delta G^\circ$  for phenanthrene radical anion cannot be evaluated because of its lack of basicity. Equilibrium acidity of the protonated anthracene radical  $ArH^\cdot$  was determined in DMSO<sup>1</sup> ( $pK_a^{ArH} = 23$ ) using the acidity of 9,10-dihydroanthracene, estimated to be 27. As a matter of fact, the value obtained experimentally by Bordwell<sup>41</sup> is equal to 30.1 and from the thermodynamic cycle proposed by Parker *et al.*<sup>1</sup> the acidity of  $ArH^\cdot$  should be equal to 20 in DMSO, and thus it is equal to 21 in DMF, as obtained from eqn. (7). The acidity in ACN ( $pK_a^{ArH} = 28.4$ ) was obtained<sup>2</sup> from experimental electro-

chemical potentials and energy change for the fragmentation of a radical measured by photoacoustic calorimetry. Using eqns. (7) and (8) one can obtain for DMF the same value as above equal to 21 and the estimated error is about 5  $pK_a$  units (taking into account the summation of errors equal to  $\pm 2 \text{ kcal mol}^{-1}$  for each  $\Delta G$  value in a thermodynamic cycle<sup>2</sup>).

The intrinsic activation barrier  $\Delta G_o^\ddagger$  for the protonation of the anthracene radical anion, found as an intercept ( $\Delta G^\circ = 0$ ) from the regression according to eqn. (14), is equal to  $59.2 \pm 0.6 \text{ kJ mol}^{-1}$ ; 95% error given is underestimated because errors in  $k_H$  and  $pK_a$  values were not taken into account. (It was assumed for the above calculation<sup>17–19</sup> that  $Z = 3 \times 10^{11} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  and  $k_H$  values were divided by a statistical factor of 2 to take into account<sup>42</sup> that a proton may attach to the carbon atom at position 9 or 10 in the anthracene radical anion). The high  $\Delta G_o^\ddagger$  value obtained, comparable with values reported for the deprotonation of radical cations of NADH analogues ( $36–67 \text{ kJ mol}^{-1}$ ),<sup>17–19</sup> can suggest that the process under consideration is similar and their dynamics is mainly governed by the homolytic bond dissociation energy.

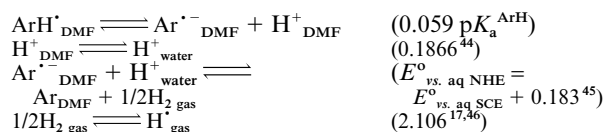
The intrinsic activation barrier is an additive property and it was thought<sup>39</sup> to be the mean of the activation barriers for two self-exchange reactions for both acid–base pairs. The last suggestion has been justified in the recent theory<sup>17–19</sup> where the deprotonation of radical cations is represented by a concerted electron and H atom transfer. However, for the reactant pair of a normal base and its conjugate acid the contribution of the ionic states prevails over the contribution of the covalent states and that self-exchange reaction has a negligibly small activation barrier.<sup>19</sup> However, this is not the case for the self-exchange reaction of a radical cation, where the homolytic dissociation (*i.e.*  $ArH^{\cdot+} \rightarrow Ar^\cdot + H^\cdot$ ) is energetically preferred.<sup>19</sup> Thus, only the homolytic bond dissociation enthalpy  $D$  of a radical cation contributes substantially to the intrinsic barrier for the deprotonation cross-reaction. Finally, the theory<sup>19</sup> expresses the intrinsic barrier as eqn. (15), where  $\lambda_o$  is the solvent reorgan-

$$\Delta G_o^\ddagger = D/4 + \lambda_o/4 \quad (15)$$

ization energy, similar to that in the original Marcus theory. Eqn. (15) was recently supported experimentally by correlations between  $\Delta G_o^\ddagger$  and  $D$  with a theoretical slope.<sup>17–19</sup>

One can expect that the proposed theory<sup>19</sup> can also be applied to a deprotonation of the neutral radical  $ArH^\cdot$ , conjugated acid of the anthracene radical anion, as well as for the reverse process of the protonation of a radical anion. For the last process a contribution of the homolytic bond dissociation in phenol, a normal acid, should be negligibly small but the  $\Delta G_o^\ddagger$  value found should be close to  $D/4$  for the  $ArH^\cdot$  radical of interest.

In the case of protonation of a radical anion the homolytic bond dissociation energy for the conjugate acid (*i.e.* the enthalpy change of the process  $ArH^\cdot \rightarrow Ar^\cdot + H^\cdot$ ) can be estimated from the thermodynamic cycle, in a similar way to that proposed by Anne *et al.*<sup>17</sup> The Gibbs free-energy changes (given in eV in parentheses) for the four steps shown in Scheme 1



**Scheme 1**

should be considered<sup>43</sup> and for the resulting process  $\Delta G^\circ = 2.476 + 0.059 pK_a^{ArH} + E^\circ(Ar/Ar^{\cdot-})$ . Assuming that entropies of formation of  $ArH^\cdot$  and  $Ar^\cdot$  are practically the same and the entropy of formation of  $H^\cdot_{gas}$  is  $27.4 \text{ eu}^{17,46}$  one can obtain  $D = 2.829 + 0.059 pK_a + E^\circ(Ar/Ar^{\cdot-}) = 2.12 \text{ eV}$  (for  $pK_a^{ArH} = 21$  and  $E^\circ(Ar/Ar^{\cdot-}) = -1.946 \text{ V vs. SCE}$ ). Thus, the contribu-

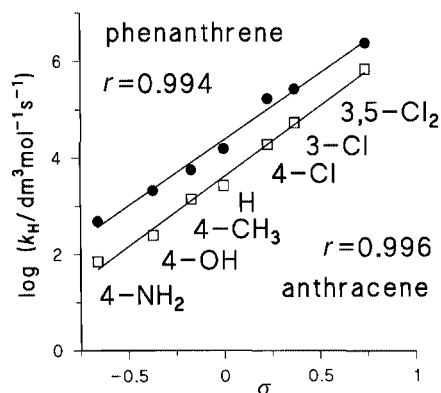


Fig. 4 Hammett plots of the rate constants for the protonation of anthracene (□) and phenanthrene (●) radical anions in DMF against  $\sigma$  values from ref. 30. Correlation coefficients  $r$  of both lines are given.

tion to the intrinsic barrier is equal to  $D/4 = 51 \text{ kJ mol}^{-1}$  which is in agreement with the experimental  $\Delta G_o^\ddagger$ . The obtained result supports the suggestion that the theory developed for the deprotonation of radical cations<sup>19</sup> can also be applied to the protonation of radical anions. Moreover, the difference between  $\Delta G_o^\ddagger$  and  $D/4$  corresponds to the expected contribution from a solvent reorganization  $\lambda_o/4$ , if the process is represented by a concerted electron and H atom transfer. For the electron self-exchange reaction between anthracene and its radical anion in DMF, experimental  $\lambda_o/4 = 0.115 \text{ eV}$ <sup>47</sup> and for the process of interest  $\lambda_o/4$  is a little lower because of the greater radius of the protonated radical. For the deprotonation of the radical cations of NADH analogues in ACN the same order of magnitude of  $\lambda_o/4$  was suggested.<sup>19</sup>

#### Hammett plots

Substituent effects on the rate constants obtained can also be described by the Hammett equation as shown in Fig. 4; substituent constants  $\sigma$  for *meta*- and *para*-substituents are given in Table 1. Significant linear correlations were obtained with the reaction constants  $\rho = 2.9 \pm 0.1$  and  $\rho = 2.7 \pm 0.1$  for the anthracene and phenanthrene radical anions, respectively. The lower  $\rho$  value (which represents a selectivity) for the second radical anion is in full agreement with the higher reactivity according to the Reactivity Selectivity Principle.<sup>20</sup> A mutual relationship between the Hammett and the Brønsted plots was discussed<sup>20,48</sup> in terms of that principle. The curvature of the Brønsted plot, indicating a smaller slope (Brønsted coefficient, *i.e.* a low selectivity) at a higher reactivity ( $k_H$  value), was interpreted on the basis of the same principle as well. On the other hand, a limited reactivity range and/or too large an intrinsic activation barrier was suggested by Pross<sup>20</sup> as a reason for the linearity of Hammett plots usually observed. Formosinho, on the basis of his intersecting-state model, also pointed out<sup>21</sup> that a transition-state bond order should be constant in the reaction series in order to obtain linear relationships; that situation was attributed<sup>22</sup> to the constant polarity of the XH bonds. The results obtained in this work (Table 1) give a unique opportunity to compare both plots of interest, shown in Fig. 3 and Fig. 4, for the same reaction series with the same  $\Delta G_o^\ddagger$ . The reactivity range is indeed shorter for the Hammett plot of the anthracene radical anions, where the point for 2,4,6-trichlorophenol is omitted because of *ortho*-substituents, but it is hard to imply that this is the only reason for no evidence of a curvature in Fig. 4, because similar behaviour is observed for the other radical anion of interest.

From a comparison of the Hammett and Brønsted plots for the rate constants  $k_H$  a simple conclusion appears that  $pK_a^{\text{PhOH}}$  also depends on the substituent constant. That relationship shown in Fig. 5 (open triangles) is the quadratic eqn. (16).

$$pK_a^{\text{PhOH}} = 18.84 (\pm 0.04) - 4.91 (\pm 0.07)\sigma - 1.3 (\pm 0.2)\sigma^2 \quad (16)$$

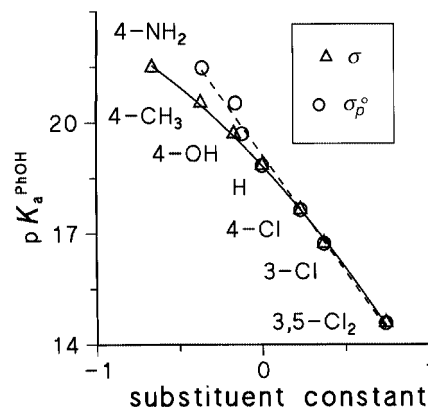


Fig. 5 Dependence of the phenols acidity  $pK_a^{\text{PhOH}}$  on the Hammett substituent constants  $\sigma$  ( $\Delta$ ) and on the normalized substituent constants  $\sigma^o$  ( $\circ$ ).

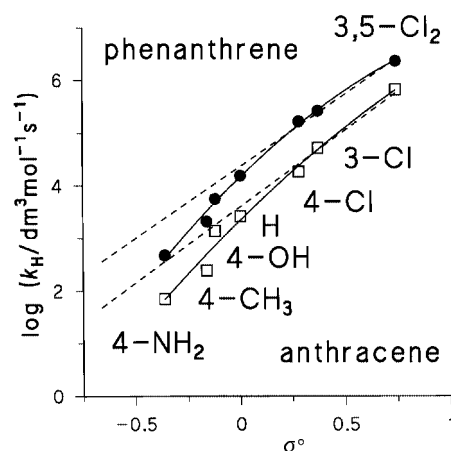


Fig. 6 Hammett plots of the rate constants for the protonation of anthracene (□) and phenanthrene (●) radical anions against the normalized substituent constant  $\sigma^o$ . Linear correlations from Fig. 4 are indicated by dashed lines.

The correlation coefficient is equal to  $R = 0.9996$ ,  $F = 2492.4$  and the quadratic term is statistically significant at the level  $\alpha = 0.01$  (for the quadratic term  $F_q = 61.2$ ). From further consideration of the signs of the regression coefficients in eqns. (9) and (16) it is evident that the quadratic terms act in opposite directions, yielding the linearity of the  $\log k_H$  against  $\sigma$  plot (Fig. 4). Taking into account that the plot shown in Fig. 5 (open triangles) illustrates a dependence between the equilibrium constants for the ionization of substituted phenols,  $pK_a^{\text{PhOH}}$ , and that of substituted benzoic acids,  $\sigma$ , in a reaction series including *para*-substituents, it is evident that the curvature obtained demonstrates the importance of the through resonance effect: for strong electron-releasing substituents, such as  $-\text{NH}_2$ , that effect occurs in the benzoic acid system (for the anion) but is unimportant in phenols. The last suggestion is supported by the use of normalized  $\sigma^o$  constants,<sup>31</sup> based on the ionization constants of phenylacetic acids, in which all through resonance interactions would be eliminated. Then, the linear correlation holds as also shown in Fig. 5 (open circles). Finally, the non-linear Hammett plots of the protonation rate constants against  $\sigma^o$  values can indeed be observed as shown in Fig. 6, with the highest selectivity (the  $\rho$  value) for *p*-amino substituent, *i.e.* for the most acidic phenol where the reactivity is the lowest, as predicted by the Reactivity Selectivity Principle. The quadratic effect is significant at the level of  $\alpha = 0.05$  ( $F_q = 8.68$ ) and only  $\alpha = 0.20$  ( $F_q = 2.5$ ) for the phenanthrene and anthracene radical anions, respectively. Nevertheless, it is evident that the linear Hammett equation, with the  $\sigma$  substituent constants observed for the rate constants of a proton transfer, is caused not only by a limited reactivity range as usually discussed in the literature<sup>20</sup>

but also by mutual compensation of non-linear terms resulting from a through-resonance effect.

In conclusion, the results obtained in this work explain the linear Hammett plots of protonation rate constants and suggest that kinetics of protonation of aromatic radical anions by a normal acid can be successfully described by the recent theory<sup>19</sup> of the concerted electron and H atom transfer.

## Experimental

Anthracene 99% from Aldrich and phenanthrene from Fluka were purified by vacuum sublimation. They were used at a concentration of 0.5 mmol dm<sup>-3</sup> and 0.1 mol dm<sup>-3</sup>, tetrabutylammonium perchlorate (Fluka) was used as a supporting electrolyte; 2-chloro-, 3-chloro-, 4-chloro- and 3,5-dichlorophenols, all Pestanal grade from Riedel-de Haën, were used as received and all other phenols were purified by vacuum sublimation. Five concentrations of phenol 0.01, 0.02, 0.03, 0.04 and 0.05 mol dm<sup>-3</sup> were normally used. *N,N*-Dimethylformamide from Merck (Uvasol grade, containing 0.028% of water) was used as received. Solutions of *p*-aminophenol are not stable in light and thus, the weighed amount of that reactant was added directly to the cell made from dark glass.

For voltammetric measurements a three-electrode cell was used consisting of a static mercury drop electrode (SMDE, Laboratorni Pristroje, Prague), a Pt counter electrode and SCE as the reference electrode. Voltammetric curves at 24 ± 1 °C were recorded with a PAR 273A potentiostat controlled by an IBM PC AT 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<sup>-1</sup> and increasing up to the value for which still  $\partial E_p/\partial \log v = -29$  mV/log unit, which normally included 8 to 20 measurements.

## Acknowledgements

Financial support from BST-623/8/99 is gratefully acknowledged.

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Paper 9/04934G