

The Protonation of the Anthracene Anion Radical in Dimethyl Sulfoxide Using Phenol and the Phenol/Phenolate Complex as Proton Sources: A Well Behaved Process

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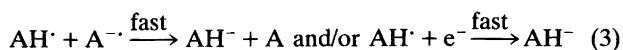
Experimental data obtained by derivative cyclic voltammetry (DCV) for the protonation of anthracene anion radical ($\text{AN}^{\cdot-}$) by phenol (PhOH) in dimethyl sulfoxide have been found to be in agreement with theoretical data for mechanism (i)–(v) with equilibrium (v)



being fast and reversible. In particular, the reaction order with respect to PhOH was observed to be unity in contrast with the values, 1.2–1.3, reported earlier for measurements carried out in *N,N*-dimethylformamide.

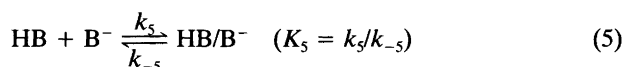
Values of the rate constant, k_{ii} , identical within experimental error, were determined in three ways; (a) under second-order conditions [$k_{\text{ii}} = (2.6 \pm 0.2) \times 10^3 \text{ M}^{-1}\text{s}^{-1}$], (b) under pseudo first-order or nearly pseudo first-order conditions [$k_{\text{ii}} = (2.48 \pm 0.07) \times 10^3 \text{ M}^{-1}\text{s}^{-1}$] and (c) by application of PhOH/PhO⁻ as the proton source using the literature value for K_{v} and assuming only PhOH to be active as the proton donor [$k_{\text{ii}} = (2.34 \pm 0.16) \times 10^3 \text{ M}^{-1}\text{s}^{-1}$].

The protonation of anion radicals ($\text{A}^{\cdot-}$) derived from alternant aromatic hydrocarbons by acids (HB) such as phenol and simple carboxylic acids is one of the most well-studied reactions in non-aqueous organic electrochemistry.^{1–16} The generally accepted mechanism is given by eqns. (1)–(4), with (2) being the rate-determining step.



Thorough kinetic studies of the protonation of the anthracene anion radical ($\text{AN}^{\cdot-}$) by phenol (PhOH) in *N,N*-dimethylformamide (DMF) have revealed the importance of the formation of the so-called homoconjugation complex, eqn. (5) [HB = PhOH], for the detailed interpreta-

tion of the kinetic data for this reaction.^{12–14} [Here, and in the following, a solidus (/) represents a hydrogen bond].



Results obtained by derivative cyclic voltammetry (DVC) at the concentration ratio, $C_{\text{PhOH}}^{\circ}/C_{\text{AN}}^{\circ} = 1$, indicated that the formation of the homoconjugation complex, PhOH/PhO⁻, may be treated kinetically as a fast and essentially irreversible reaction in DMF at the time scale of the experiment.¹³ Accordingly, the overall stoichiometry of reactions (1)–(5) is given by eqn. (6) and involves the consumption of four molecules of HB, instead of two, for each molecule of AH₂ formed.



An important experimental consequence of eqn. (6) is that the limit for the concentration ratio, $C_{\text{HB}}^{\circ}/C_{\text{A}}^{\circ}$, above which pseudo first-order conditions can safely be assumed during

DCV, is a factor of two higher than for the case without the interference from (5). This means that $C_{\text{HB}}^{\circ}/C_{\text{A}}^{\circ}$ should be at least 25.¹³ Evaluation of the reaction order in HB, as the slope of the linear regression line through the experimental points plotted as $\log v_{1/2}$ vs. $\log C_{\text{HB}}^{\circ}$,¹³ from experimental data including $v_{1/2}$ values obtained at $C_{\text{HB}}^{\circ}/C_{\text{A}}^{\circ} < \text{ca. } 25$ will lead to apparent reaction orders slightly higher than unity; ($v_{1/2}$ is the sweep rate necessary for the DCV ratio, R'_i , being equal to 0.5). For example, data obtained by digital simulation show that the apparent reaction order in HB for mechanism (1)–(5), with reaction (5) being fast and irreversible, is 1.05 when data in the range $10 \leq C_{\text{HB}}^{\circ}/C_{\text{A}}^{\circ} \leq 100$ are used.

However, the reaction order in PhOH determined by DCV in DMF has repeatedly been observed to be much higher than 1.05. Typically, values in the range 1.2–1.3 have been found, and it has been suggested¹³ that these observations reflect kinetic contributions from a reaction parallel to (2), involving protonation of $\text{AN}^{\cdot-}$ by the dimer, $(\text{PhOH})_2$, eqns. (7)–(8) [$\text{HB} = \text{PhOH}$]. Obviously, the significance of this side reaction increases with increased stoichiometric concentration of HB.



A more detailed discussion of the kinetic consequences of the hydrogen-bonding equilibria (5) and (7) should also take into account the hydrogen bond interaction between HB and the solvent.¹⁷

An obvious consequence of this competing association will be that the effect on the kinetics related to the presence of HB/B^- and $(\text{HB})_2$ is expected to decrease as the strength of the HB-solvent interaction increases. Accordingly, it might be expected that the analysis of the kinetic data obtained for protonation of $\text{AN}^{\cdot-}$ by PhOH and related reactions would be simplified considerably if the solvent, in which the experimental work was carried out, were a stronger hydrogen-bond acceptor than DMF. An obvious candidate is dimethyl sulfoxide (DMSO), which is known to be a potent hydrogen-bond acceptor and for that reason is used as a reagent (solvent) to break hydrogen bonds between dissolved species.^{18–20} In addition to this property, DMSO has the advantage of being one of the most commonly used polar, aprotic solvents for physical chemical measurements and a full array of equilibrium constants is now available for acid–base, hydrogen-bonding and ion-pairing reactions.^{21–31} However, the use of DMSO as the solvent for studies of the kinetics of protonation of anion radicals derived from simple aromatic hydrocarbons is limited.¹⁶

In this paper we report kinetic and mechanistic results for the protonation of $\text{AN}^{\cdot-}$ by PhOH in DMSO, and in addition, demonstrate the utility of the salt, Bu_4N^+ , PhOH/PhO^- , as a proton source in this type of work.

Results and discussion

The effect of the magnitude of the homoconjugation equilibrium constant, K_5 . An accurate value of K_5 for PhOH in DMF is not available, but, as mentioned above, the results of our previous investigations of the protonation of $\text{AN}^{\cdot-}$ by PhOH in DMF have shown that equilibrium (5) in this solvent strongly favors the hydrogen-bonded complex, PhOH/PhO^- , and may be treated kinetically as a fast and irreversible process under the conditions of the experiments.^{12–14} In DMSO, on the other hand, the value of K_5 for PhOH has been estimated by Bordwell and co-workers²¹ to be equal to $2.3 \times 10^3 \text{ M}^{-1}$. Comparison of the data available for compounds related to PhOH in both solvents^{20,32} shows that K_5 is on average, one order of magnitude smaller in DMSO, illustrating that DMSO is indeed a stronger hydrogen-bond acceptor than DMF. The question arising from this is to what extent back reaction (5) manifests itself kinetically during the protonation of $\text{AN}^{\cdot-}$ by PhOH in DMSO with a value of K_5 of only $2.3 \times 10^3 \text{ M}^{-1}$. In order to answer this question, values of R'_i as a function of $\log(1/v)$ were recorded by DCV under second-order conditions^{13,14} at $C_{\text{PhOH}}^{\circ} = C_{\text{AN}}^{\circ} = 1 \text{ mM}$, where the kinetic contributions from protonation of $\text{AN}^{\cdot-}$ by the dimer, $(\text{PhOH})_2$, have been demonstrated to be negligible.¹⁵ The experimental points for the sweep-rate range $0.1\text{--}100 \text{ V s}^{-1}$ are shown in Fig. 1 (circles) together with working curves obtained by digital simulation for three reaction schemes, (a) mechanism (1)–(4) with no contribution from (5), (b) mechanism (1)–(5) assuming (5) to be fast and reversible with $K_5 C_{\text{A}}^{\circ} = 2.3$, and (c) mechanism (1)–(5) assuming (5) to be fast and irreversible (See the experimental section for computational details). Comparison of the experimental data with those obtained earlier in DMF,^{13,14} which were

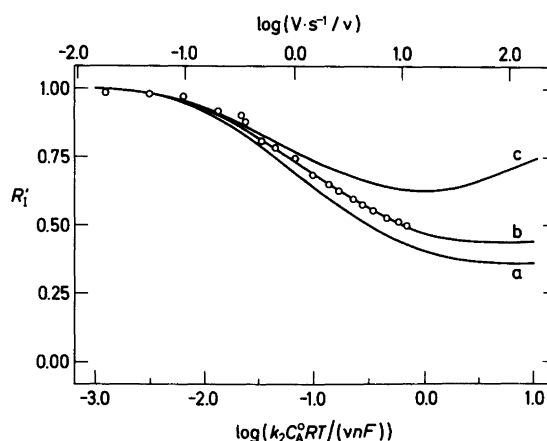


Fig. 1. Derivative cyclic-voltammetry working curves for (a) mechanism (1)–(4); (b) mechanism (1)–(5) assuming reaction (5) to be fast and reversible with $K_5 C_{\text{A}}^{\circ} = 2.3$; (c) mechanism (1)–(5) assuming reaction (5) to be fast and irreversible. In all three cases $C_{\text{HB}}^{\circ}/C_{\text{A}}^{\circ} = 1$. The experimental points (circles) are for $C_{\text{PhOH}}^{\circ} = C_{\text{AN}}^{\circ} = 1 \text{ mM}$ obtained at the sweep rates indicated by the top scale of the figure. $T = 20.4^\circ\text{C}$.

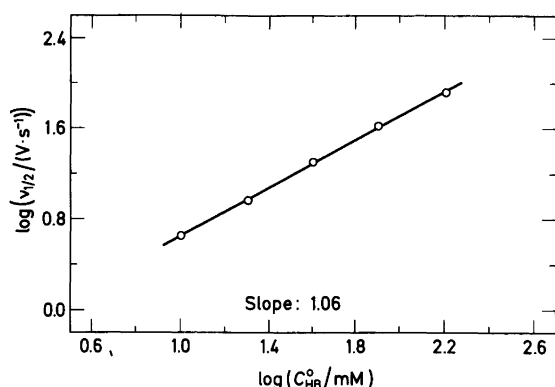


Fig. 2. Derivative cyclic-voltammetry data for the protonation of the anthracene anion radical by phenol in dimethyl sulfoxide at $T = 20.5^{\circ}\text{C}$. The apparent reaction order (see the text) is given as the slope of the linear-regression line.

found to follow curve (c), shows, as also expected, that the effect of the homoconjugation equilibrium is less pronounced in DMSO than in DMF. In fact, the experimental points for DMSO follow very closely working curve (b) based on Bordwell's value of K_5 . We take this perfect match between the experimental and theoretical data as a strong indication that reaction (5) responds as a fast equilibrium in DMSO in the sweep-rate range given above. From the experimental data and working curve (b) the rate constant for protonation, k_2 , was estimated to be $(2.6 \pm 0.2) \times 10^3 \text{ M}^{-1}\text{s}^{-1}$.

PhOH as the proton source. The major problem in previous interpretations of kinetic data obtained by DCV and linear-sweep voltammetry (LSV) for protonation of $\text{AN}^{\cdot-}$ by PhOH in DMF, was the observations of reaction orders in PhOH apparently higher than unity, which were suggested to arise primarily from the parallel reactions, (7) and (8). In order to test for the possible kinetic contributions from $(\text{PhOH})_2$ in DMSO, a DCV reaction-order analysis was carried out in the concentration range $C_{\text{PhOH}}^{\circ}/C_{\text{AN}}^{\circ} = 10\text{--}160$ at $C_{\text{AN}}^{\circ} = 1 \text{ mM}$. Fig. 2 illustrates the pleasing result that the apparent reaction order observed for PhOH is 1.06, which is almost identical with the theoretical value, 1.04 (cf. Table 1), for mechanism (1)–(5) with $K_5 = 2.3 \times 10^3 \text{ M}^{-1}$. Thus, it appears that the protonation of $\text{AN}^{\cdot-}$ in DMSO by PhOH is adequately described by eqns. (1)–(5) and that contributions from the dimer, $(\text{PhOH})_2$, are negligible in this solvent in the concentration range given above. The values of k_2 resulting from this experiment and the appropriate theoretical data (Table 1), together with additional results obtained at $C_{\text{PhOH}}^{\circ}/C_{\text{AN}}^{\circ} = 2$ and 5, are summarized in Table 2. The average values of k_2 is $(2.48 \pm 0.07) \times 10^3 \text{ M}^{-1}\text{s}^{-1}$ and we did not observe any systematic deviations from this average, which, considering that the concentration range covers almost two orders of magnitude, we take as additional evidence for the 'simplicity' of the reaction in DMSO.

Table 1. Theoretical DCV data for mechanism (1)–(5) with $K_5 C_{\text{A}}^{\circ} = 2.3$, using HB as the proton source.

$C_{\text{HB}}^{\circ}/C_{\text{A}}^{\circ}$	$k_2 C_{\text{A}}^{\circ} RT / (nFv_{1/2})^a$	$\frac{\Delta \log v_{1/2}^b}{\Delta \log C_{\text{HB}}^{\circ}}$
2	0.1150	1.50
5	0.02907	1.20
10	0.01265	1.09
20	0.005929	1.04
40	0.002874	1.02
80	0.001416	1.01
160	0.0007023	

^aThe value of the dimensionless second-order rate constant corresponding to $R_1' = 0.5$ at $E^{\circ} - E_{\text{sw}} = 0.3 \text{ V}$. ^bTwo-point slope. ^cThe apparent reaction order in C_{HB}° in the concentration range $10 \leq C_{\text{HB}}^{\circ}/C_{\text{A}}^{\circ} \leq 160$.

Table 2. Values of $v_{1/2}$ and k_2 in dimethyl sulfoxide resulting from the application of PhOH as the proton source.^a

$C_{\text{PhOH}}^{\circ}/\text{mM}$	$v_{1/2}/(\text{V s}^{-1})$	$k_2/(\text{M}^{-1}\text{s}^{-1})^b$
2	0.563	2.52×10^3
5	2.24	2.54×10^3
10	4.93	2.43×10^3
20	10.3	2.38×10^3
40	22.2	2.48×10^3
80	46.0	2.54×10^3
		av. $(2.48 \pm 0.07) \times 10^3$

^a $C_{\text{AN}}^{\circ} = 1 \text{ mM}$. The supporting electrolyte was Bu_4NBF_4 (0.1 M). $T = 20.5^{\circ}\text{C}$. ^bCalculated from $v_{1/2}$ and the theoretical data given in Table 1.

The application of the homoconjugation complex, $\text{PhOH}/\text{PhO}^{\cdot-}$, as the proton source.* The finding that the formation and dissociation of the homoconjugation complex, eqn. (5), are fast processes relative to the time-scale of the voltammetric experiments in DMSO opens the possibility of using this complex, e.g. as the tetrabutylammonium salt, as a convenient source of protons for the study of the protonation of anion radicals. Assuming that PhOH is the only active proton donor under equilibrium conditions (see below), the two reactions schemes associated with the application of PhOH, eqns. (1)–(5), and $\text{PhOH}/\text{PhO}^{\cdot-}$, eqns (5), (1)–(4), as proton sources appear to be very similar. However, when PhOH is used as the proton source under pseudo first-order conditions, the amount of PhOH captured by the $\text{PhO}^{\cdot-}$ ions formed in the proton-transfer steps has only a negligible effect on the equilibrium concentration of PhOH. This is in contrast with the situation in which $\text{PhOH}/\text{PhO}^{\cdot-}$ is used as the proton source where the con-

*In the following, we make a distinction between the *proton source*, the reagent added to the solution, and the *proton donor*, the species that actually participates in the proton-transfer step.

Table 3. Theoretical DCV data for mechanism (5), (1)–(4) with $K_5 C_A^\circ = 2.3$, using HB/B⁻ as the proton source.

$C_{\text{HB/B}^-}^\circ / C_A^\circ$	$k_2 C_A^\circ RT / (nFv_{1/2})^a$	$\frac{\Delta \log v_{1/2}^b}{\Delta \log C_{\text{HB/B}^-}^\circ}$
2	0.3451	
5	0.1387	0.99
10	0.08100	0.76
20	0.05044	0.68
40	0.03270	0.63
80	0.02178	0.59
160	0.01476	0.56

^aThe value of the dimensionless second-order rate constant corresponding to $R'_i = 0.5$ at $E^\circ - E_{\text{sw}} = 0.3$ V. ^bTwo-point slope.

centration of PhOH, due to the relatively high value of K_5 , is small and tends to decrease further during the course of the reaction owing to the continuous generation of PhO⁻. As a result of this, the protonation reaction will be subject to autoretardation when PhOH/PhO⁻ is used as the proton source.

The theoretical data for the mechanism (5), (1)–(4), given as $\log [nFv_{1/2} / (k_2 C_A^\circ RT)]$ vs. $\log C_{\text{HB/B}^-}^\circ$, are summarized in Table 3 for $K_5 C_A^\circ = 2.3$. The most striking feature of the data is that theory predicts a distinct non-linear relationship between the two parameters as reflected by the decreasing values of $\Delta \log v_{1/2} / \Delta \log C_{\text{HB/B}^-}^\circ$, and that these values are much smaller than unity although the reaction is of first order in the proton donor, HB. This is related to two factors: (i) the second-order nature of equilibrium (5), which results in a non-linear relationship between the initial concentration of HB and the stoichiometric concentration of the proton source, eqn. (9), and (ii) the continuous formation of B⁻ during the reaction.

$$[\text{HB}]_{\text{init}} = \frac{-1 + (1 + 4K_5 C_{\text{HB/B}^-}^\circ)^{1/2}}{2K_5} \quad (9)$$

From eqn. (9) it is easily seen that the value of the slope, $\Delta \log v_{1/2} / \Delta \log C_{\text{HB/B}^-}^\circ$, will be close to 0.5 at high values of $C_{\text{HB/B}^-}^\circ$.

The experimental data obtained using Bu₄N⁺, PhOH/PhO⁻ as the proton source are shown in Fig. 3 together with the working curve constructed from the theoretical data in Table 3, and again we observe a perfect match between the experimental and theoretical data. The values of k_2 calculated from these data are summarized in Table 4 for each value of $C_{\text{PhOH/PhO}^-}^\circ$ and, again, no trends in the values of k_2 are observed. The average of these values amounts to $(2.34 \pm 0.16) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, in good agreement with the results obtained for PhOH as the proton source.

Experimentally, the application of HB/B⁻ complexes with appreciable K_5 values as proton sources may be of general value in cases where the proton transfer from HB to A⁻ is too fast to allow detailed kinetic studies in the sweep-rate range of conventional DCV. Comparison of the

experimental data given in Tables 2 and 4 shows that the rate of disappearance of AN⁻ at the same concentration of the proton source is much smaller for PhOH/PhO⁻ than for PhOH. The attenuation factor, defined as $v_{1/2}(\text{HB})/v_{1/2}(\text{HB/B}^-)$ varies theoretically from 6.4 at $C_{\text{HB/B}^-}^\circ / C_A^\circ = C_{\text{HB/B}^-}^\circ / C_A^\circ = 10$, to 21 at $C_{\text{HB/B}^-}^\circ / C_A^\circ = C_{\text{HB/B}^-}^\circ / C_A^\circ = 160$, which implies that the upper attainable limit for k_2 may be increased by approximately one order of magnitude by using HB/B⁻ instead of HB as the proton source. However, it should be kept in mind that a prerequisite for the utilization of this approach is that the dissociation of HB/B⁻ may be treated kinetically as a fast equilibrium under these conditions.

The results given in Table 4 also add to the principal discussion of the nature of the microscopic proton-transfer step in cases where the proton donor is engaged in a hydrogen-bond equilibrium. Two views have been expressed.³³⁻³⁵ The first is essentially that implicitly taken above, i.e. the reaction proceeds in two steps, the first being dissociation of the hydrogen-bonded complex, followed by transfer of the proton from 'free' HB, e.g., PhOH, to the base, in the present case, AN⁻. In the alternative description, a one-

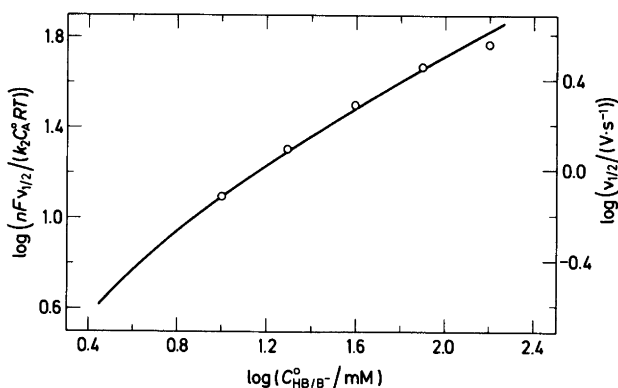


Fig. 3. Derivative cyclic voltammetry working curve for mechanism (5), (1)–(4) using HB/B⁻ as the proton source and assuming reaction (5) to be fast and reversible with $K_5 C_A^\circ = 2.3$. The experimental points (circles) are for $C_{\text{AN}}^\circ = 1$ mM obtained at the sweep rates indicated on the right-hand scale. $T = 20.7^\circ\text{C}$.

Table 4. Values of $v_{1/2}$ and k_2 in dimethyl sulfoxide resulting from the application of PhOH/PhO⁻ as the proton source.^a

$C_{\text{PhOH/PhO}^-}^\circ / \text{mM}$	$v_{1/2} / (\text{V s}^{-1})$	$k_2 / (\text{M}^{-1} \text{ s}^{-1})$
10	0.737	2.32×10^3
20	1.23	2.42×10^3
40	1.93	2.46×10^3
80	2.85	2.42×10^3
160	3.60	2.07×10^3
		av. $(2.34 \pm 0.16) \times 10^3$

^a $C_{\text{AN}}^\circ = 1$ mM. The supporting electrolyte was Bu₄NBF₄ (0.1 M). $T = 20.7^\circ\text{C}$. ^bCalculated from $v_{1/2}$ and the theoretical data given in Table 3.

step mechanism, it is assumed that the hydrogen-bonded complex is directly involved in the proton-transfer step, eqn. (10).



The observation that the rate of disappearance of $\text{AN}^{\cdot-}$ is slower for PhOH/PhO^- than for PhOH at the same concentration of the proton source, is not in itself sufficient to distinguish between the two mechanisms, since it may be explained by either of them. In the two-step mechanism one may rationalize the slow reaction observed for PhOH/PhO^- as being due to the low equilibrium concentration of 'free' PhOH , and in the one-step mechanism the low rate may be explained by the lower acidity of PhOH/PhO^- as compared with PhOH . What is important is the relationship between the stoichiometric concentrations of the proton sources and the $v_{1/2}$ values, i.e. the reaction-order plots. If it is assumed that the reaction between $\text{AN}^{\cdot-}$ and PhOH/PhO^- takes place entirely through the one-step mechanism, eqn. (10), the associated reaction order plot is expected to be very similar to that observed for PhOH as the proton source (Fig. 2). In particular, it is expected that the slope approaches unity as the values of $C_{\text{PhOH/PhO}^-}^{\circ}$ increases, due to the analogous rate laws (11) and (12).

$$-d[\text{AN}^{\cdot-}]/dt = 2k_2[\text{AN}^{\cdot-}][\text{PhOH}] \quad (11)$$

$$-d[\text{AN}^{\cdot-}]/dt = 2k_{10}[\text{AN}^{\cdot-}][\text{PhOH/PhO}^-] \quad (12)$$

However, as mentioned above, the experimental data fit very closely the working curve for the two-step mechanism, the slope of which approaches 0.5 with increasing values of $C_{\text{PhOH/PhO}^-}^{\circ}$. Although the experimental data analysed in this manner seem to be in agreement only with the two-step mechanism, this agreement is not sufficient evidence to exclude completely contributions from the one-step mechanism, since possible systematic deviations from a non-linear working curve are not easily detected. Examination of the numerical data given in Table 4 is much more reliable for this purpose. If the protonation of $\text{AN}^{\cdot-}$ proceeds with significant contributions from the one-step mechanism, the values of k_2 calculated from the theoretical data for the two-step mechanism are expected to increase with increased stoichiometric concentration of PhOH/PhO^- owing to the increased value of the concentration ratio $[\text{PhOH/PhO}^-]/[\text{PhO}^-]$ according to eqn. (9). The fact that we do not observe this trend in our data seems to indicate that the direct proton transfer from undissociated PhOH/PhO^- to $\text{AN}^{\cdot-}$ constitutes only a minor pathway.

Experimental

Reagents, electrodes, cells and instrumentation. Anthracene, phenol and tetrabutylammonium tetrafluoroborate were of the same origin as previously described.¹² The solutions of tetrabutylammonium tetrafluoroborate (0.1

M) in dimethyl sulfoxide (Fluka, purum) were passed through a column filled with neutral alumina (Woelm, W200) immediately before the measurements were made. The tetrabutylammonium salt of the phenol/phenolate anion was prepared by mixing stoichiometric amounts of tetrabutylammonium hydroxide (40% in water, Fluka) and phenol, and then removing the water by azeotropic distillation with cyclohexane under reduced pressure.

The electrodes, cells and instrumentation were as reported earlier.¹²

Digital simulations. The simulations were carried out in double precision on an HP 9826 A computer. The simulation method was essentially the same as previously described.^{12,15} For the mechanisms including equilibrium (5) as a fast and reversible reaction, the kinetic part of the simulation was carried out in two individual steps involving the establishment of equilibrium (5) in each volume element followed by evaluation of the irreversible kinetic terms using the integrated rate law. It was deemed unnecessary to re-establish equilibrium (5) after the evaluation of the irreversible kinetic terms in each time step since preparatory work demonstrated that this approach resulted in theoretical data indistinguishable from those obtained as described above.

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