The Source and the Resolution of the Controversy Regarding the Interpretation of Linear Sweep Voltammetry Data for the Protonation of Anthracene Anion Radical by Phenol

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The results of a number of linear sweep voltammetry (LSV) studies have appeared to be contradictory and have resulted in controversy. It is shown that there are no inconsistencies in the published data when all data are treated in the same manner. The apparent inconsistencies noted earlier are artefacts in the nature of the data treatment. Two important points which have not previously been recognised contribute to the confusion surrounding the interpretation of the data. These are i) the reaction of anthracene anion radical with phenol does not fulfill the requirements for a purely kinetic LSV process under the experimental conditions used and ii) the stoichiometry of the reaction is $2\ A^{\cdot -} + 4\ PhOH \rightarrow$ products. The latter results from the fact that the $2\ PhO^-$ formed in the reaction remove 2 PhOH by virtue of the large association constant between these species. Point ii) is important in the LSV data interpretation in that the assumption of pseudo first order in $A^{\cdot -}$ is not valid over the entire range of [PhOH] used in the experimental work. Theoretical calculations were carried out taking points i) and ii) into account and excellent agreement with experimental data was found for the simple ECE_h mechanism, the essential feature of which is rate determining irreversible protonation.

Few mechanisms in organic electrochemistry and ion radical chemistry have been the subject of so much work and such a vigorous discussion as that for the reaction between anthracene anion radical, $A^{\cdot -}$, and phenol, PhOH, in *N,N*-dimethylformamide, DMF.[1–14] In spite of all these efforts, the details of the reaction are still not agreed upon and not only the interpretation,[8–14] but also the validity of certain experimental results based on newly developed techniques has been drawn into the debate.[10] The mechanism of protonation of $A^{\cdot -}$ by PhOH is in itself not of sufficient interest to merit so much attention, but it has served as a valuable model for the study of protonation of anion radicals derived from aromatic hydrocarbons in aprotic solvents in general, and we feel that the difficulties encountered during the studies cited above do reflect chemistry of general interest and at the same time that the results are highly relevant for the future applications of electroanalytical techniques in the study of these and related ion radical reactions.

In order for the reader fully to appreciate the discussion which follows, we have found it necessary to give a rather detailed summary of the previous work. However, we will restrict ourselves mainly to results and arguments based on one technique, linear sweep voltammetry, LSV, and leave the implications of measurements from cyclic voltammetry, derivative cyclic voltammetry, DCV, and double potential step chronoamperometry, DPSC, to a forthcoming publication.

The reaction between $A^{\cdot -}$ and PhOH in DMF has been used as a model for testing new voltammetric measurement techniques.[5–7] Until 1981,[2,4,6] it was generally believed that the reaction is adequately described by the following sequence of steps:

$$A + e^- \rightleftarrows A^{\cdot -} \tag{1}$$

$$A^{\cdot -} + PhOH \xrightarrow{k_2} AH^{\cdot} + PhO^- \tag{2}$$

$$AH^{\cdot} + A^{\cdot -} \xrightarrow{k_3} AH^- + A \tag{3}$$

$$AH^- + PhOH \xrightarrow{k_4} AH_2 + PhO^- \tag{4}$$

Mechanism I.

$$-d[A^{\cdot -}]/dt = 2k_2[A^{\cdot -}][PhOH] \tag{5}$$

with rate law (5) reflecting that (2) is rate determining. This reaction scheme is commonly known as an ECE_h, an ECE (nuance) or a DISP 1 mechanism. However, the exact nature of the chemical steps is not obvious from these abbreviations and in the following we will refer to this reaction sequence as mechanism I and only use DISP 1 in reference to work by Savéant and coworkers who introduced this terminology.[15] The assignment of the mechanism was primarily based on results from DPSC measurements[4,6] and it appeared to be supported by LSV and DCV results as well.[4–7] The experimental values of $dE_p/d\log v$[4,5] and $dE_p/d\log C^{\circ}_{PhOH}$[6] were observed to be close to the theoretical values required by mechanism I, −29.1 mV and +29.1 mV at 20 °C, respectively, where E_p is the peak potential, v is the voltage sweep rate and C°_{PhOH} is the bulk concentration of PhOH. The value of $d\ln R'_I/d\ln(1/v)$ was found[7] to be equal to −0.379 in good agreement with the theoretical value (−0.378), where R'_I is the ratio of the anodic and cathodic derivative peak heights. The second order rate constant, k_2, was estimated[4] by DPSC at C°_{PhOH} = 10 mM and assuming pseudo first order conditions to be equal to 4500 $M^{-1}\,s^{-1}$ in good agreement with values determined later by help of the same technique (4000 $M^{-1}\,s^{-1}$),[6] (4800 $M^{-1}\,s^{-1}$)[13] and by DCV (5300 $M^{-1}\,s^{-1}$)[6] as well as LSV (4800 $M^{-1}\,s^{-1}$).[13]

However, the extensive work[8,9] carried out in the laboratory of one of the authors during the development of DCV and derivative LSV resulted in a quantity of data apparently incompatible with the previously accepted simple view on the mechanism. The inconsistencies can be summarized as follows: 1) The numerical values of $dE_p/d\log v$ were in general found to be much smaller than the 29.1 mV required by a reaction first order in $A^{\cdot -}$ and to decrease with decreasing concentration of PhOH approaching in the limit, C°_{PhOH} = 10 mM, the value, 19.4 mV, corresponding to a reaction second order in $A^{\cdot -}$.[8,9] The same trend was observed when 2,6-dimethylphenol was used as the proton donor.[8] 2) This apparent change in reaction order of $A^{\cdot -}$ was paralleled by a similar trend in the DCV slope, $d\ln R'_I/d\ln(1/v)$.[8] 3) The reaction order in PhOH as measured by DCV was observed to change gradually from values larger than one at low PhOH concentrations (10–40 mM) to approximately one at higher PhOH concentrations (100 mM).[8] 4) The reaction was found to be inhibited by addition of phenolate ion, PhO^-.[8]

Reaction orders in both $A^{\cdot -}$ and PhOH in the range between one and two as well as the inhibition of the reaction by PhO^- forced the discussion of the mechanism to include the reverse steps (2) and (3) and it was concluded that although the reaction appeared to follow the simple rate law (5) at high values of C°_{PhOH}, it was necessary to involve all three steps, (2)–(4), in determining the rate at low values of C°_{PhOH}.[8,9]

This suggested mechanism transition was sharply criticized by Savéant and coworkers [10] and in a very broad discussion four limiting mechanisms were furthermore ruled out. The ECE_{rev} [(2) being reversible and (3) being substituted by the electrode process: $AH^{\cdot} + e^- \rightarrow AH^-$] and the DISP 3 [(2) and (3) being reversible and (4) being rate determining] were ruled out since E_p was found not to be significantly affected by variations of the substrate concentration, C°_A, while both the ECE_{rev} and the DISP 3 pathways require non-zero values of the slope, $dE_p/d\log C^{\circ}_A$, −29.1 mV for ECE_{rev} and −19.4 mV for DISP 3, both numbers referring to unbuffered solutions. Furthermore, the two mechanisms require $dE_p/d\log C^{\circ}_{PhOH}$ values higher than the ~29 mV observed,[10] the theoretical values being 58.2 mV (ECE_{rev}) and 38.8 mV (DISP 3). (For the sake of clarity, the theoretical values of

Table 1. Variations of the LSV peak potentials for the limiting mechanisms (at 20 °C). Data from Ref. 10.

	ECE_{rev}	ECE_{irr}	DISP 1	DISP 2	DISP 3
Unbuffered media					
$(\mathrm{d}E_p/\mathrm{dlog}v)$/mV	−29.1	−29.1	−29.1	−19.4	−19.4
$(\mathrm{d}E_p/\mathrm{dlog}C^{\circ}_{A})$/mV	−29.1	0	0	0	−19.4
$(\mathrm{d}E_p/\mathrm{dlog}C^{\circ}_{PhOH})$/mV	58.2	29.1	29.1	19.4	38.8
Buffered media					
$(\mathrm{d}E_p/\mathrm{dlog}v)$/mV	−29.1	−29.1	−29.1	−19.4	−19.4
$(\mathrm{d}E_p/\mathrm{dlog}C^{\circ}_{A})$/mV	0	0	0	19.4	0
$(\mathrm{d}E_p/\mathrm{dlog}C^{\circ}_{PhOH})$/mV	29.1	29.1	29.1	0	19.4

the LSV slopes for five limiting cases are summarized in Table 1). It was also emphasized that due to an estimated difference between $E^{\circ}_{A/A^{\cdot-}}$ and $E^{\circ}_{AH^{\cdot}/AH^{-}}$ of at least 600 mV, the minimum value of the equilibrium constant for the electron transfer reaction (3) is 10^{10} which together with the assumption that k_3 is close to the diffusion controlled limit calls for an unacceptably low value of k_4 in order that the DISP 3 limiting case could be operating. Two other limiting mechanisms, the ECE_{irr} [(3) being replaced by $AH^{\cdot} + e^{-} \rightarrow AH^{-}$] and the DISP 2 [(2) being reversible and (3) being rate determining] were ruled out by the data obtained by DPSC. It was concluded [10] that the reaction follows without ambiguity the kinetics predicted by the DISP 1 limiting mechanism in the concentration regions investigated, *i.e.* $C^{\circ}_{A} = 0.5$ to 2 mM and $C^{\circ}_{PhOH} = 10$ to 100 mM with no appreciable contributions from other possible limiting mechanisms. At this point we do wish to emphasize that nobody, to the best of our knowledge, has recently advocated contributions from the ECE_{rev} or ECE_{irr} cases or that the reaction proceeds according to the DISP 2 or DISP 3 limiting cases.

However, later results[11] and reanalysis of old data[12] have revealed that the value of $\mathrm{d}E_p/\mathrm{dlog}C^{\circ}_{PhOH}$ in fact was larger than 29.1 mV, which seemed to indicate that the reaction order in PhOH was higher than one in disagreement with the simple DISP 1 mechanism. This result was rationalized[13] in terms of mechanism II involving the formation of 1:1 and 1:2 complexes between $A^{\cdot-}$ and PhOH as depicted in eqns. (1), (6)–(9). Dependent on the competition between steps (7) and (8–9) this mechanism gives rise to reaction orders in PhOH varying between one and two and accordingly $\mathrm{d}E_p/\mathrm{dlog}C^{\circ}_{PhOH}$ values between 29.1 mV and 58.2 mV.*

$$A + e^{-} \rightleftharpoons A^{\cdot-} \qquad (1)$$

$$A^{\cdot-} + PhOH \overset{K_6}{\rightleftharpoons} A^{\cdot-}/PhOH \qquad (6)$$

$$A^{\cdot-}/PhOH \overset{k_7}{\rightleftharpoons} AH^{\cdot} + PhO^{-} \qquad (7)$$

$$A^{\cdot-}/PhOH + PhOH \overset{K_8}{\rightleftharpoons} A^{\cdot-}/2PhOH \qquad (8)$$

$$A^{\cdot-}/2PhOH \overset{k_9}{\rightleftharpoons} AH^{\cdot} + PhOH + PhO^{-} \qquad (9)$$

Mechanism II.

$$-\mathrm{d}[A^{\cdot-}]/\mathrm{d}t = k_7K_6[A^{\cdot-}][PhOH] (1 + (k_9/k_7)K_8[PhOH]) \qquad (10)$$

The most extensive set of LSV data pertaining to this reaction was presented at a recent conference[14] and are summarized in Table 2. The data confirmed the earlier reported[8,9] trend in the numerical value of $\mathrm{d}E_p/\mathrm{dlog}v$ which was found to change from ~23 mV at $C^{\circ}_{PhOH} = 10$ mM to ~27 mV at $C^{\circ}_{PhOH} = 40$ mM. Addition of increasing amounts of PhO^{-} caused these values to decrease, the minimum in the series, ~11 mV, being reached at $C^{\circ}_{PhOH} = 10$ mM and $C^{\circ}_{PhO^{-}} = 8$mM. The latter result demonstrated that PhO^{-} does indeed participate in determining the over-all

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*There is some confusion in terminology in Ref. 10 and 13. Both mechanism I and mechanism II are labelled as DISP 1 although the rate laws differ substantially.

Table 2. LSV data for the reduction of anthracene in DMF in the presence of different phenols and the corresponding phenolate ions.

ArOH	*p*-Chlorophenol					Phenol					*p*-Methoxyphenol			
$C^{\circ}_{\mathrm{ArOH}}$ mM	10	20	40	10–20	20–40	10	20	40	10–20	20–40	20	40	80	20–40
$C^{\circ}_{\mathrm{ArO^-}}$ mM	$\Delta E_p/\Delta\log v$[a]			$\Delta E_p/\Delta\log C^{\circ}_{\mathrm{ArOH}}$[b]		$\Delta E_p/\Delta\log v$[a]			$\Delta E_p/\Delta\log C^{\circ}_{\mathrm{ArOH}}$[b]		$\Delta E_p/\Delta\log v$[a]			$\Delta E_p/\Delta\log C^{\circ}_{\mathrm{ArOH}}$[b]
0	−24.9	−26.0	−26.7	36.5	36.5	−22.9	−25.7	−27.0	36.2	34.2	−21.2	−25.1	−27.0	25.6
1	−24.7	−26.0	−26.5	41.5	37.2	−21.7	−25.3	−26.7	40.2	35.5	−20.6	−24.9	−26.9	29.9
2	−24.6	−25.9	−26.2	44.2	39.5	−21.1	−25.2	−26.7	39.9	37.5	−19.8	−24.7	−26.9	29.9
4	−23.9	−25.9	−26.4	52.2	41.2	−18.7	−24.5	−26.6	46.8	38.9	−18.4	−24.2	−26.5	37.2
8	−22.3	−25.6	−26.2	64.4	48.5	−10.9	−23.2	−26.4	65.8	45.8	−14.6	−23.7	−26.5	46.5

[a] Two point slopes at v = 0.1 and 1 V · s^{-1}, respectively. [b] Two point slopes in the indicated concentration region.

rate of the reaction[8] in disagreement with the simple mechanism I, which predicts the LSV slopes to be insensitive to the concentration of PhO$^-$. The earlier observation[11–13] that dE_p/dlog$C^{\circ}_{\mathrm{PhOH}}$ was larger than 29.1 mV was also confirmed by this study. Comparison of the results obtained by application of the two *p*-substituted phenols as proton donors with those for PhOH demonstrated that the trend in dE_p/dlogv with increasing concentration of the phenol apparently is related to the acidity of the proton donor and is least pronounced for the strongest acid, *p*-chlorophenol. However, the values are, even for this compound, still 2–4 mV from that required by mechanism I. Furthermore, it should be noticed that the slope, dE_p/dlog$C^{\circ}_{\mathrm{ArOH}}$ with ArOH representing any of the phenols, is markedly dependent on the concentration of ArO$^-$. The slope was found to increase with increasing concentration of ArO$^-$ and exceeds in the limit of these measurements, $C^{\circ}_{\mathrm{ArOH}}$ = 10 to 20 mM and $C^{\circ}_{\mathrm{ArO-}}$ = 8 mM, even the value, 58.2 mV, for a mechanism which is second order in ArOH. This, and the observation that dE_p/dlog$C^{\circ}_{\mathrm{PhOH}}$ appeared to decrease with increasing $C^{\circ}_{\mathrm{PhOH}}$, cannot be explained within the framework of the complex-mechanism (II) proposed by Savéant and coworkers.[13] No direct mechanistic conclusions were drawn at the time of presentation[14] of these data except that the reaction between A$^{\cdot-}$ and PhOH in DMF features some obscure complications not accounted for by mechanism I.

Until now it has been taken for granted that the theoretical slopes for LSV mechanism analysis derived by Savéant and coworkers and summarized in Table 1 are in fact applicable to the present chemical system in the concentration ranges already mentioned. However, when comparing experimental data in form of dE_p/dlogv, dE_p/dlogC°_{A} and dE_p/dlog$C^{\circ}_{\mathrm{PhOH}}$ with the theoretical values given in Table 1, it should be kept in mind that the latter have been derived using two basic assumptions: 1) The reaction is under purely kinetic control and 2) the reaction takes place under pseudo first order conditions, which in the present case implies that rate law (5) may be written as (11). Furthermore, with regard to the effect

$$-\mathrm{d}[A^{\cdot-}]/\mathrm{d}t = 2k_2C^{\circ}_{\mathrm{PhOH}}[A^{\cdot-}] = 2k_2'[A^{\cdot-}] \qquad (11)$$

of deliberately added PhO$^-$ it has tacitly been assumed that 3) the stoichiometric concentration of

Table 3. Linear sweep voltammetry data for the reduction of anthracene in DMF in the presence of phenol.[a]

C°_{PhOH}/ mM	ν = 100 mV·s^{-1}				ν = 200 mV·s^{-1}				ν = 400 mV·s^{-1}				ν = 1000 mV·s^{-1}						
	$-E_p$	$-E_{p/2}$	$E_p-E_{p/2}$	I_p	$-E_p$	$-E_{p/2}$	$E_p-E_{p/2}$	I_p	$-E_p$	$-E_{p/2}$	$E_p-E_{p/2}$	I_p	$-E_p$	$-E_{p/2}$	$E_p-E_{p/2}$	I_p	$\frac{dE_{p/2}}{d\log\nu}$	$\frac{dE_p}{d\log\nu}$	$\frac{dE_p}{d\log\nu}$[b]
0	581.0	523.8	−57.2	18.4									580.1	523.6	−56.5	56.4			
10	554.9	499.5	−55.4	32.3	562.3	506.6	−55.7	44.1	568.6	512.7	−55.9	59.3	578.8	519.7	−59.1	84.5	−20.1	−23.7	−23.7
20	546.2	492.1	−54.1	38.3	552.9	499.7	−53.2	51.9	559.7	506.2	−53.5	71.1	571.6	515.0	−56.6	104	−22.7	−25.3	−25.9
40	536.2	483.3	−52.5	45.6	543.1	490.4	−52.7	62.8	549.5	498.1	−51.4	86.4	562.4	508.8	−53.6	132	−25.6	−25.9	−25.9
100	521.7	470.4	−51.3	46.5	528.6	476.9	−51.7	63.2	535.5	484.6	−50.9	89.2	547.4	496.2	−51.2	139	−25.6	−25.6	−26.3
$\frac{dE_{p/2}}{d\log C^{\circ}_{PhOH}}$		29.2				30.0				28.2				23.5					
$\frac{dE_p}{d\log C^{\circ}_{PhOH}}$		33.3				33.7				33.2				31.5					
$\frac{dE_p}{d\log C^{\circ}_{PhOH}}$[b]		34.3				33.4				32.5				29.8					

[a] All potentials are in mV at 21°C. The potentiostat bias was −1.350 V *vs.*Ag/Ag$^+$ (DMF). Peak currents, I_p, are given in arbitrary units. C°_A = 1 mM. [b] Slopes based on data obtained by differentiation. All other measurements were carried out as described in the experimental section.

PhO^-, $C^{\circ}_{PhO^-}$, does indeed reflect the effective solution concentration of this species and that addition of PhO^- to the voltammetric solutions does not affect the effective concentration of PhOH. The aim of this paper is to demonstrate that none of these three criteria are fulfilled by the reaction between $A^{\bar{\cdot}}$ and PhOH in DMF in the concentration ranges, $C^{\circ}_{A} = 0.5$ to 2 mM and $C^{\circ}_{PhOH} = 10$ to 100 mM, and to show that the remaining controversy regarding the experimental data, the dE_p/dlogv values, has its origin in the data treatment only. As far as point 1) is concerned it should be pointed out that the reaction under the above conditions *does* fall in the purely kinetic region as defined by Nadjo and Savéant,[16] *but* that the boundaries between the kinetic zones now require some adjustment.

Results and discussion

In order to resolve the controversy we carried out a new, more fine-meshed set of LSV experiments. Values of E_p were obtained both by the derivative technique[6] and a more elaborate direct acquisition procedure (see the experimental section for details) similar to that recently reported[17] which also allowed values of $E_{p/2}$ and I_p, the peak current, to be recorded accurately. The data are summarized in Tables 3 and 4 and will be brought into the discussion at the appropriate places.

Table 4. The dependence of the peak potential on substrate concentration during LSV of anthracene in the presence of phenol.[a]

C°_{A}/mM	$-E_p$ (v = 100 mV/s)	$-E_p$ (v = 1000 mV/s)
0.25	539.3	567.2
0.50	539.2	565.8
1.0	540.0	566.2
2.0	540.3	565.5
3.0	540.3	564.9
$\dfrac{dE_p}{d\log C^{\circ}_{A}}$	−1.1	1.7

[a]All potentials are in mV at 21 °C. The potentiostat bias was −1.350 v *vs.* Ag/Ag$^+$ (DMF). $C^{\circ}_{PhOH} = 25$ mM.

The origin of the apparent controversy

An important problem, which is of general concern to workers in this area, is: Why does the LSV technique apparently give different results for the same chemical system when applied by two different research groups? The answer is very simply that it does not! Originally Savéant and coworkers claimed[4,10] that their LSV data were in agreement with mechanism I (DISP 1), a conclusion based on the observation that the experimental data appeared to give a good fit to curves of E_p *vs.* logv and E_p *vs.* $\log(vF/(RTC^{\circ}_{PhOH}))$ calculated for that mechanism. The dependence of E_p directly on $\log C^{\circ}_{PhOH}$ was apparently not evaluated, which was probably deemed unnecessary since a plot of E_p *vs.* $\log C^{\circ}_{PhOH}$ for this particular mechanism is equivalent with the plot of E_p *vs.* $\log(vF/(RTC^{\circ}_{PhOH}))$. Both curves are predicted by theory to be straight lines with the same numerical slope, 29.1 mV, in the region where the reaction is under purely kinetic control. However, as we have already mentioned in the introduction, a re-analysis of the data[13] gave rise to a $dE_p/d\log C^{\circ}_{PhOH}$ value which was considerable higher than 29.1 mV although the value was not explicitly given. However, from Fig. 3 in Ref. 10 it is easy to estimate that the value is close to 35 mV in good agreement with the value we find (Tables 2 and 3). Now, how is it possible that the very same data which originally[10] were found to be in agreement with a $dE_p/\log C^{\circ}_{PhOH}$ slope of 29.1 mV are now, after "close inspection",[13] in agreement with a value approximately 6 mV higher? The answer to this question is related to the value of dE_p/dlogv. The two plots of E_p *vs.* $\log C^{\circ}_{PhOH}$ and E_p *vs.* $\log(vF/(RTC^{\circ}_{PhOH}))$ are equivalent if and only if the value of dE_p/dlogv is equal to −29.1 mV. We invariably found (Table 2) and still do find (Table 3) that the numerical value of this slope at low PhOH concentrations is significantly smaller than 29.1 mV and that it approaches this values with increasing PhOH concentrations and we will now demonstrate that the data obtained by Savéant and coworkers[10] do show the same trend when they are allowed to tell their own story instead of being forced to fit the working curves for mechanism I. In Fig. 1 is shown two plots of their data for $C^{\circ}_{PhOH} = 10$ mM (a) and $C^{\circ}_{PhOH} = 100$ mM (b), respectively. Since the raw data were not given, it was necessary to read them from Fig. 3 in Ref. 10, which appeared

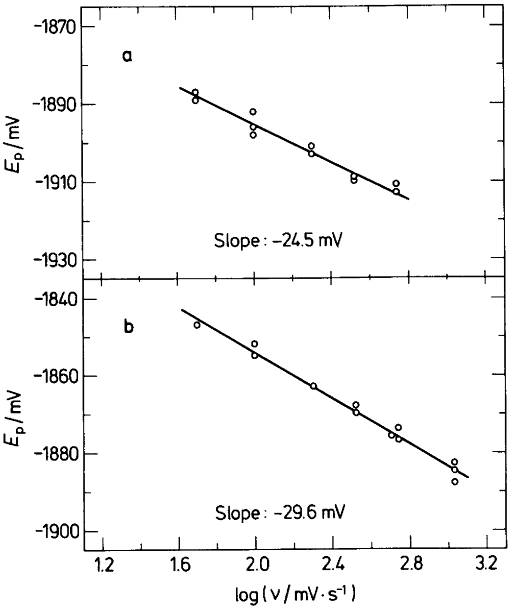

Fig. 1. Evaluation of dE_p/dlogv for the reduction of A in the presence of PhOH by linear regression. C^o_{PhOH} = 10 mM (a) and 100 mM (b). Data from Fig. 3 in Ref. 10.

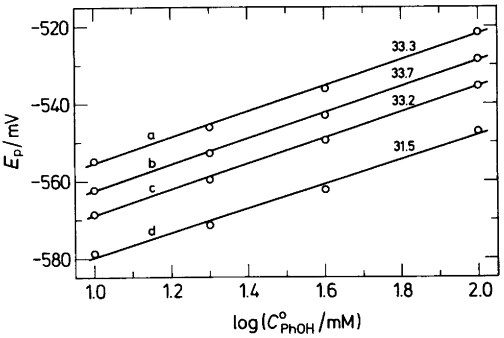

Fig. 3. Evaluation of dE_p/dlogC^o_{PhOH} for the reduction of A in the presence of PhOH by linear regression. v = 100 mV·s^{-1} (a), 200 mV·s^{-1} (b), 400 mV·s^{-1} (c) and 1000 mV·s^{-1} (d). Same data as in Fig. 2.

to be a procedure without risk due to the relatively large scale used in that plot. As it is evident from our treatment of the data, the value of dE_p/dlogv at C^o_{PhOH} = 10 mM (a) amounts to only −24.5 mV, while the data obtained at C^o_{PhOH} = 100 mM (b) results in a slope close to the theoretical −29.1 mV. This difference in the slopes is exactly why it was possible to overlook the high dE_p/dlogC^o_{PhOH} value in the first place. The low numerical values of dE_p/dlogv counterbalance to some extent the high dE_p/dlogC^o_{PhOH} values in a plot of E_p *vs.* log(vF/(RTC^o_{PhOH})). This point is convincingly demonstrated in Figures 2–4 where in this case our new experimental data (Table 3) are plotted as E_p *vs.* logv (Fig.2), E_p *vs.* logC^o_{PhOH} (Fig. 3) and finally as E_p *vs.* log(vF/(RTC^o_{PhOH})) (Fig. 4). Despite the fact that the slopes of the two first plots (Fig. 2 and Fig. 3) are significantly different from those required by mechanism I under purely kinetic conditions, the slope in Fig. 4 is apparently in perfect agreement with the predicted value. We find this an instructive example of how the fine structure in experimental data

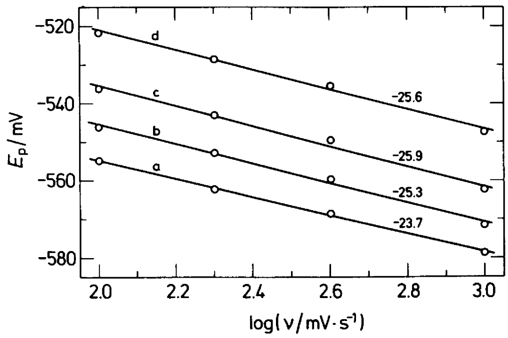

Fig. 2. Evaluation of dE_p/dlogv for the reduction of A in the presence of PhOH by linear regression. C^o_{PhOH} = 10 mM (a), 20 mM (b), 40 mM (c) and 100 mM (d). Data from Table 3.

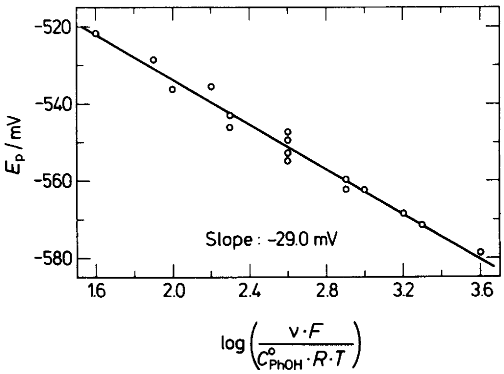

Fig. 4. Evaluation of dE_p/dlog(vF/RTC^o_{PhOH}) by linear regression. Same data as in Fig. 2.

may be masked by application of a mixed parameter analysis which is only really suitable for theoretical data.

However, when all the published and unpublished LSV data for the reaction between $A^{\cdot -}$ and PhOH are gathered, it is obvious that the trend in the data we have just described, especially for the sweep rate dependence, occasionally is less pronounced[13] or vanishes.[5] We attribute this to mainly two origins. Firstly our experience is that experimental data for proton transfer reactions in aprotic media like DMF in general may be extremely difficult to reproduce to a high level of precision, a problem we have not encountered during studies of other ion radical reactions. We believe that this is primarily due to uncontrolled amounts of protic impurities in the aprotic solvents which in the case of DMF could be dimethylamine and water. Since we are dealing with rates and not equilbiria even small amounts of impurities capable of participating in acid-base reactions may affect the over-all rate considerably. Secondly, if the data are only processed numerically and not plotted, the presence of a bad data point may escape attention resulting in erroneous LSV slopes. This is a particularly severe problem in LSV analysis, since in most cases only relatively few points are in general used to define the slopes. The latter problem was apparently the reason why a set of d$E_{p/2}$/dlogv values (~ −30 mV) resulting from one of the first LSV studies[5] of the reaction in question seemed to be in agreement with mechanism I. A plot of the data reported in Ref. 5 shows, however, that the E_p values at $v = 245.8$ mV·s^{-1} are inconsistent with the others, probably due to a sweep rate calibration error, and discrimination of this point causes the slope of d$E_{p/2}$/dlogv (average of 5 series) to change from −30.4 mV ($r = -0.991$) to −24.9 mV ($r = -0.9999$) at C°_{PhOH} equal to 38.5 mM.

It has been impled [10,12] that the differences observed in LSV slopes from various sources may arise from errors inherent in the differentiation procedure. This possibility has been thoroughly ruled out.[17,18] LSV measurements were made on the protonation of 1,1-diphenylethylene anion radical by methanol, a reaction which exhibits the characteristics of a purely kinetic process, by various measurement methods. It was found that dE_p/dlogv and d$E_{p/2}$/dlogv, where only the former used data obtained by the differentiation procedure, were very nearly identical.[18] Furthermore, dE_p/dlogv derived from E_p data obtained by differentiation did not differ from that derived from E_p evaluated by a more detailed procedure such as that described in the experimental section.[17] This procedure involves the direct analysis of current-potential curves with E_p evaluated by fitting the data in the region of the current maximum to a polynomial equation and differentiation.[17]

The conclusion that the critique of the experimental methods has no basis is further substantiated by the data in Table 3. It is easily seen that the reaction between $A^{\cdot -}$ and PhOH is no exception in this respect and that the data obtained by the differentiation procedure do not deviate in any significant manner from those obtained by the more elaborate direct processing of the experimental current-voltage curves.

Thus, the general conclusion as far as the experimental LSV slopes are concerned is that the numerical value of dE_p/dlogv changes from 21–24 mV at $C^{\circ}_{PhOH} = 10$ mM to 26–29 mV at $C^{\circ}_{PhOH} = 100$ mM and that dE_p/dlogC°_{PhOH} is in the range 33–36 mV at low sweep rates, values which appear to be independent of their instrumental as well as geographical origin. The task at hand is now to explain these values in terms of a mechanism.

The effect on dE_p/dlogv of the chemical reaction not being under purely kinetic conditions. The data in Table 2 suggested that the magnitude of the trend in dE_p/dlogv with increasing values of C°_{PhOH} was associated with the acidity of the phenol, which again obviously is related to the overall rate of the reaction. The relative rates as measured by DCV and the pK_a-values for the three phenols are summarized in Table 5. Although the pK_a-values refer to aqueous solution, there is little doubt that their relative magnitude may be transferred to DMF considering that the

Table 5. Relative rates of protonation of $A^{\cdot -}$ by ArOH measured by DCV.[a]

ArOH	$v_{\frac{1}{2}}$/V·s^{-1}	pK_a[b]
p-MeO	3.3	10.20
p-H	10.5	9.98
p-Cl	180	9.42

[a] In DMF containing Bu_4NBF_4 (0.1 M) at 21 °C; $C^{\circ}_A = 1$ mM; $C^{\circ}_{ArOH} = 10$ mM. [b] In aqueous solution.[19]

Table 6. Theoretical linear sweep voltammetry data and values of $\Delta E_p/\Delta \log C_A^o$ and $\Delta E_{p/2}/\Delta \log C_A^o$ for mechanism I at 25 °C.

	$k_2C^o_{PhOH}RT/(vnF) = 1.3$							$k_2C^o_{PhOH}RT/(vnF) = 13$						
C^o_{PhOH}/C^o_A	E_p-E_o mV	$E_p-E_{p/2}$ mV	i_p[a]	$\Delta E_p/\Delta \log C_A^o$[c]		$\Delta E_{p/2}/\Delta \log C_A^o$[c]		E_p-E_o mV	$E_p-E_{p/2}$ mV	i_p[a]	$\Delta E_p/\Delta \log C_A^o$[c]		$\Delta E_{p/2}/\Delta \log C_A^o$[c]	
∞[b]	−25.4	−57.6	0.722					3.2	−51.0	0.890				
100	−25.4	−57.7	0.721	0.1	0.2[d]	0.1	0.4[e]	3.1	−51.1	0.888	−0.4	−1.1[d]	0	0.05[e]
40	−25.3	−57.7	0.720	0.1		0.3		3.0	−51.3	0.886	−0.9		0.1	
20	−25.3	−57.7	0.717	0.3		0.5		2.7	−51.5	0.883	−1.6		0.1	
13	−25.2	−57.8	0.714	0.7		0.4		2.4	−51.9	0.878	−2.1		0.3	
10	−25.2	−57.8	0.712	0.8		0.5		2.1	−52.1	0.875	−2.8		0.2	
8	−25.1	−57.8	0.709	0.9		1.3		1.9	−52.4	0.871	−3.4		0.6	
6	−25.0	−57.9	0.705	1.1		1.4		1.4	−52.9	0.864	−4.3		0.9	
5	−24.9	−57.9	0.702					1.1	−53.3	0.858				

[a] Normalized peak current. [b] Assuming pseudo first order conditions and $k_2'RT/(vnF) = 1.3$ and 13, respectively. [c] Two point slopes calculated from the raw simulation data before round off. [d] Value of $dE_p/d\log C_A^o$ by linear regression. [e] Value of $dE_{p/2}/d\log C_A^o$ by linear regression.

Table 7. Theoretical values of $\Delta E_p/\Delta \log v$ and $\Delta E_{p/2}/\Delta \log v$ at 25 °C.[a]

	mechanism I		mechanism III	
C^o_{PhOH}/C^o_A	$\Delta E_p/\Delta \log v$	$\Delta E_{p/2}/\Delta \log v$	$\Delta E_p/\Delta \log v$	$\Delta E_{p/2}/\Delta \log v$
∞[b]	−28.6	−22.0	−28.6	−22.0
100	−28.5	−21.9	−28.4	−21.9
40	−28.3	−21.9	−28.0	−21.8
20	−28.0	−21.8	−27.3	−21.7
13	−27.6	−21.7	−26.6	−21.6
10	−27.3	−21.7	−26.0	−21.5
8	−27.0	−21.6	−25.4	−21.4
6	−26.5	−21.5	−24.4	−21.4
5	−26.0	−21.5	−23.8	−21.4

[a] Two point slopes calculated from the peak and half-peak potential data given in Tables 6 and 8. [b] Assuming pseudo first order conditions and $k_2'RT/(vnF) = 1.3$ and 13, respectively.

structural changes are small and restricted to the *p*-position. Thus, the data in Table 5 clearly indicate, as expected, that the more acidic the phenol, the faster the reaction. That the trends in the dependence of the peak potential on the sweep rate apparently is associated with the reaction rate brought into question whether or not the protonation of A^- by PhOH in the concentration range investigated was under purely kinetic control. What is meant by this term is that the rate of the chemical process is fast compared to the experimental technique, which in LSV analysis usually is expressed through a dimensionless parameter, for the present reaction $k_2C^o_{PhOH}RT/(vnF)$ or $k_2'RT/(vnF)$, which should be a large number, in the ideal (limiting) case infinitely large. When the value of $k_2'RT/(vnF)$ is allowed to decrease, in principle from infinity, towards zero, the relationships given in Table 1 will change their magnitude and the value of $k_2'RT/(vnF)$ at which the deviations from the limiting slopes will be experimentally detectable depends only on the precision of the measurement technique.

The values of k_2 referred to in the introduction were all calculated under the assumption that the experimental conditions allowed the reaction to be treated kinetically as a pseudo first order process and that the reaction followed mechanism I. Although, as will be demonstrated later, these conditions are not strictly fulfilled, the k_2 values given are certainly of the right order of magnitude. At $C^{\circ}_{\mathrm{PhOH}}$ = 10 mM, which was the concentration at which the rate constant was determined originally,[4] the average value of k_2' is approximately 50 s^{-1} taking all the reported values into account. The sweep rate range normally applicable for LSV measurements is 0.1 $\mathrm{V \cdot s^{-1}}$ to 1 $\mathrm{V \cdot s^{-1}}$[9] and accordingly the parameter $k_2'RT/(vnF)$ will take values close to 13 and 1.3, respectively, at room temperature. We will use these numbers as the basis for the discussion to follow.

The first question which now arises is: Are these values sufficiently large that the reaction can be considered to be under purely kinetic conditions? To answer this and other related questions to follow, we carried out an extensive series of calculations based on digital simulation. The interested reader may find the details in the special section on this subject. Theoretical data for mechanism I assuming pseudo first order conditions, *i.e.* that $k_2' = k_2C^{\circ}_{\mathrm{PhOH}}$ which in principle corresponds to $C^{\circ}_{\mathrm{PhOH}}/C^{\circ}_{\mathrm{A}} = \infty$, are summarized in Tables 6 and 7 (upper lines). The values of the two point slopes $\Delta E_p/\Delta \log v$ and $\Delta E_{p/2}/\Delta \log v$ (v = 0.1 $\mathrm{V \cdot s^{-1}}$ and 1 $\mathrm{V \cdot s^{-1}}$) amount to −28.6 mV and −22.0 mV, respectively (Table 7) as compared to the limiting −29.6 mV (the potential values given in the following refer all to t = 25 °C). While the difference between the actual and the limiting value of $\Delta E_p/\Delta \log v$ is close to the detection limit, the corresponding difference related to the half-peak potential is certainly far from it. This relatively large, and at first surprising, difference between the deviation of the two slopes from the limiting value is related to the changing shape of the voltammetric peak in this transition zone as illustrated by the data in Table 6. The values of the half-peak width, E_p–$E_{p/2}$, and the normalized peak current, i_p, vary from −57.6 mV and 0.722 at 1 $\mathrm{V \cdot s^{-1}}$ to −51.0 mV and 0.890 at 0.1 $\mathrm{V \cdot s^{-1}}$, respectively, while the limiting values for these two parameters are −47.8 mV and 0.992.[16] Thus, it is evident that the system, especially at 1 $\mathrm{V \cdot s^{-1}}$, is far from being under purely kinetic control.

The additional effect of the chemical reactions not being strictly under pseudo first order conditions. The next question to be answered is: Are the values of $C^{\circ}_{\mathrm{PhOH}}$ in the range 10 to 100 mM at C°_{A} = 1 mM sufficiently large to cause the system to be under pseudo first order conditions, and if not, how much is $dE_p/d\log v$ affected by this additional deviation from the ideal behavior? To test for this, simulations were carried out in which the parameter $k_2'RT/(vnF)$ was substituted by $k_2C^{\circ}_{\mathrm{PhOH}}RT/(vnF)$, but keeping the values, 13 and 1.3, constant. The results are summarized in Tables 6 and 7. Compared to the −28.6 mV for mechanism I when $C^{\circ}_{\mathrm{PhOH}}/C^{\circ}_{\mathrm{A}} = \infty$, the value of $\Delta E_p/\Delta \log v$ decreases numerically with decreasing $C^{\circ}_{\mathrm{PhOH}}/C^{\circ}_{\mathrm{A}}$ reaching −26.0 mV at $C^{\circ}_{\mathrm{PhOH}}/C^{\circ}_{\mathrm{A}}$ = 5, which slope is not less than 3.6 mV from the limiting value. The slope calculated from the $E_{p/2}$ values is less affected by the increasingly larger deviation from the pseudo first order conditions in going from $C^{\circ}_{\mathrm{PhOH}}/C^{\circ}_{\mathrm{A}} = \infty$ to 5, which is related to the much smaller conversion at this potential (related to time of reaction).

Inspection of Table 1 shows that the peak potential is predicted to be unaffected by the substrate concentration, C°_{A}, for mechanism I (entrance DISP 1) in the limiting case. The deviations from this zero slope in the actual case are only small and may take positive as well as negative values. When the simulated values are treated as if they were results of an experiment, *i.e.* plotted as E_p *vs.* $\log C^{\circ}_{\mathrm{A}}$ the resulting slopes amount to 0.2 mV and −1.0 mV at 1 V/s and 0.1 V/s, respectively. The values of E_p–$E_{p/2}$ indicate that the broadness of the peak increases with decreasing values of $C^{\circ}_{\mathrm{PhOH}}/C^{\circ}_{\mathrm{A}}$ even at v = 1 V/s at which sweep rate the peak in fact is broader than that for a reversible couple (−56.6 mV). This trend is, however, in good agreement with data published by Nadjo and Savéant[16] on mechanism I under strictly pseudo first order conditions (DISP 1), which show that E_p–$E_{p/2}$ with increasing values of $k_2'RT/(vnF)$ passes through a maximum, −60.8 mV at $k_2'RT/(vnF)$ close to 0.35, before decreasing towards the limiting value, −47.8 mV. Thus, with decreasing $C^{\circ}_{\mathrm{PhOH}}/C^{\circ}_{\mathrm{A}}$ values, the shape of the peak reflects the over-all reduced rate of the reaction, which is also illustrated by the simultaneously diminishing peak current.

The theoretical data discussed so far were primarily calculated in order to get an estimate of the magnitude of the errors introduced by assuming the reaction to be fast and under pseudo first order conditions in the absence of additional chemical complications. However, the problems introduced in this way may to some extent be eliminated by the proper choice of experimental conditions and are as such partly in the hands of the experimentalist. This is not the case for third and in our opinion most important contribution to the deviation from ideal behavior, the complexation of PhO^- by PhOH.

The effect of formation of the homoconjugate complex, $PhOH/PhO^-$ on the LSV slopes. An important point in understanding the reaction between $A^{\cdot-}$ and PhOH in DMF in particular and acid base reactions of this and related types in aprotic solvents in general is the actual nature of the negatively charged species in the presence of proton donors. The solvents commonly applied for electrochemical measurements are all characterized by a low ability to solvate negatively charged ions. This is reflected in relatively modest acity numbers[20] which are 0.30, 0.34 and 0.37 for DMF, dimethylsulfoxide (DMSO) and acetonitrile (MeCN), respectively. Accordingly, it is to be expected that PhO^- in DMF containing an excess PhOH is present not as the free ion, but rather as a $PhOH/PhO^-$ complex [eqn. (12)]. Whether or not the formation of such a complex is of any relevance in the present context depends entirely on the magnitudes of k_{12} and K_{12}. In case they both are large the effect on the actual concentration of PhOH in solution is that four instead of two molecules disappear for each two molecules of $A^{\cdot-}$ reacting, as illustrated by the stoichiometry of the over-all reaction (eqn. 13). In this case, the assumption of pseudo first order

$$\mathrm{PhOH} + \mathrm{PhO^-} \underset{k_{-12}}{\overset{k_{12}}{\rightleftharpoons}} \mathrm{PhOH/PhO^-}$$

$$K_{12} = k_{12}/k_{-12} \tag{12}$$

$$2\,\mathrm{A^{\cdot-}} + 4\,\mathrm{PhOH} \rightarrow \mathrm{AH_2} + \mathrm{A} + 2\,\mathrm{PhOH/PhO^-} \tag{13}$$

conditions in the concentration range of the experiment is obviously even worse than before.

Unfortunately equilibrium (12) appears not to have been quantitatively characterized in DMF. However, K_{12} is known[21] in DMSO to be close to $10^3\ \mathrm{M^{-1}}$, and with the almost identical acity numbers for DMF and DMSO referred to above, it seems reasonable to assume that K_{12} in DMF is of a similar magnitude. The limiting mechanism for which the formation of $PhOH/PhO^-$ may be considered as fast and irreversible is the scheme for which we have carried out the most extensive set of calculations including values of $\mathrm{d}E_p/\mathrm{dlog}v$ and $\mathrm{d}E_p/\mathrm{dlog}C^{\circ}_{\mathrm{PhOH}}$. This mechanism, which consists of steps (1)–(4) and (14) will in the following be termed mechanism III. Since the effect of the additional equation (14) is to further decrease the effective concentration of PhOH, it is obviously expected that incorporation of this equation in the calculations will further accentuate the trends already described for $\mathrm{d}E_p/\mathrm{dlog}v$ and $\mathrm{d}E_p/\mathrm{dlog}C^{\circ}_{\mathrm{A}}$; this was indeed observed to be the case (Tables 7 and 8). Inspection of Table 7 shows that at $C^{\circ}_{\mathrm{PhOH}}/C^{\circ}_{\mathrm{A}} = 5$, the sweep rate dependence of the peak potential is now only -23.8 mV, while the value based on the half-peak potential as before is only moderately affected.

$$\mathrm{A} + e^- \rightleftharpoons \mathrm{A^{\cdot-}} \tag{1}$$

$$\mathrm{A^{\cdot-}} + \mathrm{PhOH} \xrightarrow{k_2} \mathrm{AH^{\cdot}} + \mathrm{PhO^-} \tag{2}$$

$$\mathrm{AH^{\cdot}} + \mathrm{A^{\cdot-}} \xrightarrow[\text{fast}]{k_3} \mathrm{AH^-} + \mathrm{A} \tag{3}$$

$$\mathrm{AH^-} + \mathrm{PhOH} \xrightarrow[\text{fast}]{k_4} \mathrm{AH_2} + \mathrm{PhO^-} \tag{4}$$

$$\mathrm{PhOH} + \mathrm{PhO^-} \xrightarrow[\text{fast}]{k_{14}} \mathrm{PhOH/PhO^-} \tag{14}$$

Mechanism III

The dependence of E_p on the substrate concentration calculated as $\mathrm{d}E_p/\mathrm{dlog}C^{\circ}_{\mathrm{A}}$ in the region $C^{\circ}_{\mathrm{PhOH}}/C^{\circ}_{\mathrm{A}} = 100$ to 8 amounts now to -2.1 mV and 0.5 mV at $v = 0.1\ \mathrm{V \cdot s^{-1}}$ and $1\ \mathrm{V \cdot s^{-1}}$, respectively and is so large that it is expected to be observed experimentally. The data in Table 4 confirm that a small negative slope is observed at $v = 0.1\ \mathrm{V \cdot s^{-1}}$, while the data obtained at $1\ \mathrm{V \cdot s^{-1}}$ result in a small positive slope. However, much more important is the comparison of the trends in the theoretical data in Tables 9 and 10 with those of the experimental data in Table 3. Before going into a discussion of the results we would like to

Table 8. Theoretical linear sweep voltammetry data and values of $\Delta E_p/\Delta\log C^0_A$ and $\Delta E_{p/2}/\Delta\log C^0_A$ for mechanism III at 25 °C.

	$k_2C^0_{PhOH}RT/(\nu nF) = 1.3$					$k_2C^0_{PhOH}RT/(\nu nF) = 13$				
C^0_{PhOH}/C^0_A	E_p-E_0 mV	$E_p-E_{p/2}$ mV	i_p[a]	$\Delta E_p/\Delta\log C^0_A$[c]	$\Delta E_{p/2}/\Delta\log C^0_A$[c]	E_p-E_0 mV	$E_p-E_{p/2}$ mV	i_p[a]	$\Delta E_p/\Delta\log C^0_A$[c]	$\Delta E_{p/2}/\Delta\log C^0_A$[c]
∞[b]	−25.4	−57.6	0.722			3.2	−51.0	0.890		
100	−25.3	−57.7	0.720	0.1	0.3	3.0	−51.2	0.887	−0.8	0.1
40	−25.3	−57.7	0.717	0.3	0.6	2.7	−51.5	0.883	−1.8	0.2
20	−25.2	−57.8	0.712	0.6 }0.4[d]	1.0 }0.7[e]	2.1	−52.1	0.875	−3.0 }−2.1[d]	0.4 }0.3[e]
13	−25.1	−57.9	0.706	1.1	1.5	1.6	−52.8	0.866	−4.1	0.8
10	−24.9	−57.9	0.702	1.7	2.0	1.1	−53.3	0.858	−4.8	1.2
8	−24.8	−57.9	0.697	2.3	2.3	0.6	−53.9	0.848	−5.5	2.2
6	−24.5	−57.9	0.688	3.4	3.4	−0.1	−54.9	0.831	−5.2	3.7
5	−24.2	−57.9	0.681			−0.5	−55.6	0.817		

[a]Normalized peak current. [b]Assuming pseudo first order conditions and $k_2'RT/(\nu nF) = 1.3$ and 13, respectively. [c]Two point slopes calculated from the raw simulation data before round off. [d]Value of $dE_p/d\log C^0_A$ by linear regression. [e]Value of $dE_{p/2}/d\log C^0_A$ by linear regression.

Table 9. Theoretical linear sweep voltammetry data and values of $\Delta E_p/\Delta\log C^0_{PhOH}$ and $\Delta E_{p/2}/\Delta\log C^0_{PhOH}$ for mechanism III at 25 °C.

	$k_2C^0_ART/(\nu nF) = 0.13$					$k_2C^0_ART/(\nu nF) = 1.3$				
C^0_{PhOH}/C^0_A	E_p-E_0 mV	$E_p-E_{p/2}$ mV	i_p[a]	$\Delta E_p/\Delta\log C^0_{PhOH}$	$\Delta E_{p/2}/\Delta\log C^0_{PhOH}$[c]	E_p-E_0 mV	$E_p-E_{p/2}$ mV	i_p[a]	$\Delta E_p/\Delta\log C^0_{PhOH}$[c]	$\Delta E_{p/2}/\Delta\log C^0_{PhOH}$[c]
∞[b]	–	−47.8	0.992	29.6	29.6		−47.8	0.992	29.6	29.6
320	18.3	−49.6	0.932	30.1	27.6					
226.3	13.8	−50.0	0.921	30.3	27.3					
160	9.2	−50.4	0.908	30.4	26.8					
113.1	4.7	−51.0	0.893	30.6	26.2					
80	0.1	−51.6	0.875	30.4	25.1	30.0	−49.2	0.950	31.0	28.6
56.57	−4.5	−52.4	0.855	30.0	23.9	25.3	−49.5	0.942	31.2	28.2
40	−9.0	−53.4	0.831	29.5 }28.0[d]	22.4 }20.9[e]	20.6	−50.0	0.931	31.7 }32.0[d]	27.9 }27.5[e]
28.28	−13.5	−54.4	0.804	28.2	20.4	15.9	−50.6	0.919	32.3	27.4
20	−17.7	−55.6	0.773	25.8	17.9	11.0	−51.3	0.903	32.7	26.6
14.14	−21.6	−56.8	0.739	22.2	14.9	6.1	−52.2	0.883	33.0	25.6
10	−24.9	−57.9	0.702	17.2	11.6	1.1	−53.3	0.858	32.1	23.7
7.07	−27.5	−58.7	0.663	11.3	8.4	−3.7	−54.6	0.826	29.3	20.9
5	−29.2	−59.2	0.625			−8.4	−55.9	0.786		

[a]Normalized peak current. [b]Assuming pseudo first order conditions and $k_2'RT/(\nu nF) = \infty$; values from ref. 16. [c]Two point slopes calculated from the raw simulation data before round off. [d]Value of $dE_p/d\log C^0_{PhOH}$ by linear regression. [e]Value of $dE_{p/2}/d\log C^0_{PhOH}$ by linear regression.

Table 10. Theoretical values of $\Delta E_p/\Delta \log v$ and $\Delta E_{p/2}/\Delta \log v$ for mechanism III at various values of C°_{PhOH}/C°_A and $k_2 C^\circ_A RT/(vnF)$ = 0.13 and 1.3, respectively.[a]

C°_{PhOH}/C°_A	$\Delta E_p/\Delta \log v$	$\Delta E_{p/2}/\Delta \log v$
80	−29.2	−27.5
56.57	−29.8	−26.9
40	−29.6	−26.2
28.28	−29.4	−25.6
20	−28.7	−24.4
14.14	−27.7	−23.1
10	−26.0	−21.4
7.07	−23.8	−19.7
5	−21.1	−17.8

[a] Two point slopes calculated from the data in Table 9.

emphasize that the theoretical data as already mentioned were calculated using an average estimate of the rate constant, and that no attempt was made to fit these data to the particular set of experimental results given in Table 3. In the discussion we will mainly focus on the similarity in the trends in the two data sets and in particular for $dE_p/d\log C^\circ_{PhOH}$ and $dE_p/d\log v$.

Due to the fact that the chemical system at low PhOH concentrations is not under strictly pseudo first order conditions, the values of E_p–E_o will be more negative than those in the absence of this complication. Using again the data by Nadjo and Savéant[16] as our reference, the effect at fx C°_{PhOH} = 10 mM and v = 0.1 V · s^{-1} amounts to approximately 2 mV. Now, with increasing PhOH concentrations the effective consumption of PhOH during the reaction will percentage wise be smaller and as a result the system will approach purely pseudo first order conditions. The effect is that the lag in E_p–E_o will be gradually compensated for resulting in $dE_p/d\log C^\circ_{PhOH}$ values larger than 29.6 mV. The effect reaches its maximum in the concentration range used in this study giving rise to a slope of 32.0 mV (Table 9) in the region between C°_{PhOH} = 10 and 80 mM in satisfactory agreement with the experimental values, the average of which amounts to 33.9 mV (Table 3) at that particular sweep rate. The values related to $E_{p/2}$ are less affected because of the simultaneous narrowing of the peak. In the same concentration region the theoretical data results in $dE_{p/2}/d\log C^\circ_{PhOH}$ = 27.5 mV as compared to the experimental value 29.2 mV. At v = 1 V · s^{-1} the effect is smaller resulting in a theoretical value of $dE_p/d\log C^\circ_{PhOH}$ of only 28.0 mV, which should be compared to the experimental average of 30.7 mV. For $dE_{p/2}/d\log C^\circ_{PhOH}$ at the same sweep rate the corresponding values were found to be equal to 20.9 mV and 23.5 mV, respectively. In all cases the same trends are observed experimentally as theoretically. With the experimental basis for the suggestion of mechanism II including a 1:2 complex between A^- and PhOH in mind it is of interest to notice that $dE_p/d\log C^\circ_{PhOH}$ values up to at least 32–33 mV may be observed for a system which is strictly first order in PhOH.

If we now turn to the dependence of E_p on the sweep rate, the predominant trend in the theoretical as well as the experimental data is that $dE_p/d\log v$ is far from the limiting 29.6 mV at low concentrations of PhOH and that this value gradually is approached as the concentration is allowed to increase. In fact at C°_{PhOH} = 10 mM, the experimental slope, −23.7 mV, is closer to that for the limiting case for a reaction second order in A^-, −19.7 mV, than that for a first order process, −29.6 mV. Comparison of the theoretical and the experimental data on a more absolute basis, demonstrates that the experimental slopes do not reach the limiting value as quickly as predicted by the data in Table 10, although the difference between the values related to E_p and $E_{p/2}$ becomes smaller as expected. When the experimental data are plotted as E_p (or $E_{p/2}$) *vs.* logv it becomes evident that the plot is slightly curved, and that the slope reaches the largest numerical value at the higher sweep rates. That the experimental data at the lowest sweep-rates apparently are less reliable is supported by the values of E_p–$E_{p/2}$ (Table 3) which are expected to reflect that the peak becomes more and more narrow when the sweep-rate is decreased. This is also observed in the experimental data when going from v = 1.0 V · s^{-1} to 0.4 V · s^{-1}, but the effect seems to level off and occasionally the peak becomes even a little broader on lowering the sweep-rate. We suspect that this problem is related to adsorption of phenol[1] or species produced during the chemical reaction, which is expected to play a more important role at the lower sweep rates where the conversion is highest.

Finally we would like to focus on the magnitude of the peak currents. In the limiting case, the value of I_p is expected to be 2.22 times that of

Table 11. Values of $\Delta E_p/\Delta \log C^{o,corr}_{PhOH}$ in so-called buffered solution corrected for the stoichiometric changes imposed by the formation of PhOH/PhO$^-$.[a]

ArOH	*p*-Chlorophenol		Phenol		*p*-Methoxyphenol
C^{o}_{PhOH}/mM	10–20	20–40	10–20	20–40	20–40
$C^{o}_{PhO^-}$/mM	$\Delta E/\Delta \log C^{o,corr}_{ArOH}$		$\Delta E/\Delta \log C^{o,corr}_{PhOH}$		$\Delta E_p/\Delta \log C^{o,corr}_{ArOH}$
0 (0)	36.5 (10–20)	36.5 (20–40)	36.2 (10–20)	34.2 (20–40)	25.6 (20–40)
1 (~0)	38.5 (9–19)	35.9 (19–39)	37.3 (9–19)	34.2 (19–39)	28.8 (19–39)
2 (~0)	37.8 (8–18)	36.6 (18–38)	34.1 (8–18)	34.8 (18–38)	27.7 (18–38)
4 (~0)	36.9 (6–16)	35.2 (16–36)	33.1 (6–16)	33.2 (16–36)	31.8 (16–36)
8 (~0)	24.9[b] (2–12)	34.3 (12–32)	25.5[b] (2–12)	32.4 (12–32)	32.9 (12–32)
	average: 36.5±1.3		average: 34.4±1.5		

[a] Data from Table 2. Values in parenteses are concentrations (mM) corrected for formation of PhOH/PhO$^-$. [b] Not included in the average. Cf. the text.

the reversible system in the absence of chemical follow-up reactions. The theoretical data shows that neither this criterion is met by the present system. At $C^{o}_{PhOH} = 10$ mM and $v = 0.1$ V · s^{-1} and 1.0 V · s^{-1} the ratios of the theoretical values to that for the reversible couple, 0.4463, amounts to only 1.57 and 1.92, respectively, in acceptable agreement with the experimental values of 1.50 and 1.76.

Having discussed the influence of the formation of the PhOH/PhO$^-$ complex on the LSV data obtained under conditions where PhO$^-$ was not deliberately added, we now return to the data in Table 2. The results given in that Table were obtained under what was believed to be buffered conditions, which in the conventional sense of the word was meant to imply that the solutions contained PhOH and PhO$^-$ in proportions given by the stoichiometric concentrations. However, with the essentially irreversible formation of PhOH/PhO$^-$ from PhOH and PhO$^-$ in mind, it is quite obvious that the buffered conditions were never established. The effect of adding PhO$^-$ is rather to diminish the effective concentration of PhOH with an amount equivalent to that of the added PhO$^-$. Thus, in Table 2 the readings $C^{o}_{PhO^-} = 4$ mM and $C^{o}_{PhOH} = 10$–20 mM should rather read $C^{o}_{PhO^-} = {\sim}0$ mM and $C^{o}_{PhOH} = 6$–16 mM and accordingly the effective change in the PhOH concentration did correspond to a factor of 2.7 instead of the factor of 2.0 assumed in the calculation of $\Delta E_p/\Delta \log C^{o}_{PhOH}$. Taking this into account the value is reduced from 46.8 mV given in Table 2 to 33.1 mV. Values of $\Delta E_p/\Delta \log C^{o,corr}_{PhOH}$, where $C^{o,corr}_{PhOH}$ represents the effective concentration of PhOH corrected for the PhOH/PhO$^-$ formation, are summarized in Table 11. The increasing trend in the numbers with increasing $C^{o}_{PhO^-}$ disappears and with the exceptions of the values at $C^{o}_{PhO^-} = 8$ mM and $C^{o}_{PhOH} = 10$–20 mM, the slopes are now all in excellent agreement with those listed in Table 3 (experimental data) and Table 2 (theoretical data). The average of nine values (Table 11) amounts to 34.4 mV, exactly the value obtained from the new data (Table 3) by the same derivative technique. At $C^{o}_{PhO^-} = 8$ mM and $C^{o}_{PhOH} = 10$–20 mM, the slopes were for both *p*-chlorophenol and phenol significantly smaller than 34 mV after the correction. This is due to the very slow reaction at $C^{o,corr}_{PhOH} = 2$–12 mM and inspection of the theoretical data in Table 9 shows that this trend in the data is expected in that concentration region.

Conclusions

The primary conclusion of the two studies[8,9] which provided the fuel for the controversy over the interpretation of LSV data for the protonation of A$^{\cdot-}$ by phenol in DMF was that this is another example of a rather complex mechanism for an ion radical reaction. We concur with this conclusion but find that when proper consideration is taken of the correct stoichiometry and it is recognised that previous work was not always under conditions expected 1) to give rise to purely kinetic LSV waves or 2) to fulfill the requirements of pseudo first order kinetics, the deviations between the experimental and theoretical data are no longer apparent. Within the limits of experimental error and the reproducibility of measurements, all of the experimental LSV data are consistent with the theoretical data for mechanism III.

We conclude that mechanism III accounts for the LSV data but in no way mean to imply that this is *the* mechanism of the protonation of anthracene anion radical by phenol in aprotic solvents. Other mechanisms, involving the same overall stoichiometry, may give rise to rate laws which are sufficiently similar to that for mechanism III to render assignment on the basis of LSV alone a very uncertain process.

With regard to mechanism III, it should be emphasized that although the proton transfer reaction (2) is not formulated as reversible, this is not meant to imply that we consider this step to be inherently irreversible, but only that the back reaction of (2) is not allowed to manifest itself kinetically under the reaction conditions as revealed by LSV. Neither have we meant to indicate that the transfer of a proton from PhOH to $A^{\overline{\cdot}}$ is a simple process microscopically. On the contrary, we find it plausible that in this case, like in other proton transfer processes,[22-25] an initial 1:1 complex is formed as an intermediate during the course of the reaction. However, a mechanism scheme including such a complex, $A^{\overline{\cdot}}$/PhOH in the present case, will lead to a rate expression which cannot be distinguished by the LSV technique from that for mechanisms I and III, and accordingly the formation of an intermediate 1:1 complex will not be reflected in data obtained by this technique. This is not the case when the mechanism scheme includes the formation of a 1:2 complex, $A^{\overline{\cdot}}$/2PhOH (mechanism II). The reaction order in PhOH will now be between one and two, which predicts $dE_p/d\log C^{\circ}_{\mathrm{PhOH}}$ values larger than 29.6 mV, and it was the observation of values close to 35 mV which was the experimental basis for this suggestion originally.[13] However, our theoretical treatment of mechanism III, which is strictly first order in PhOH, has shown that values up to at least 33 mV can be observed solely due to the fact that the reaction is not in the purely kinetic region and that the experiments do not secure strictly pseudo first order conditions. The latter is further emphasized by the formation of the PhOH/PhO$^-$ complex. Thus, in our opinion there is not left much room for the suggestion of participation of a 1:2 complex between $A^{\overline{\cdot}}$ and PhOH during the present reaction.

The earlier conclusion[8,9] that the observation of $dE_p/d\log v$ values which were numerically smaller than that for a first order reaction in $A^{\overline{\cdot}}$ reflected contributions from a rate law second order in $A^{\overline{\cdot}}$ suffers similarly. Our theoretical results on mechanism III demonstrate that values all the way down to 20 mV are fully compatible with a first order reaction when again the rate and the stoichiometry of the reaction are taken properly into account. The results of the theoretical work presented in this paper are not in any way unexpected, but the considerations behind it were not sufficiently seriously considered in the previous work on this reaction mechanism.

The high equilibrium constant for the formation of the PhOH/PhO$^-$ complex is probably not unique in this field of chemistry and therefore questions the relevance of theoretical data for so-called buffered conditions as long as the reactions are carried out in aprotic solvents like DMF, DMSO and MeCN.

Experimental

Reagents, electrodes, cells. Anthracene was from Rhône-Poulenc, Prolabo, *pur,* and used as received. Phenol was from Ferak and distilled at reduced pressure prior to use. The substituted phenols were from Fluka, *purum* or *puriss,* and used as received. Tetrabutylammonium tetrafluoroborate was precipitated from an aqueous solution of the hydrogen sulfate (Hässle) by addition of fluoboric acid (Riedel–de Haën, 50 % solution in water). The product was dissolved in dichloromethane and the resulting solution was washed several times with water and finally dried over molecular sieves. The pure salt was obtained by precipitation with diethyl ether, filtration and drying. Solutions of tetrabutylammonium tetrafluoroborate in DMF (Ferak, distilled at reduced pressure prior to use) were passed through a column filled with neutral alumina (Woelm, W 200) immediately before the voltammetric measurements were made.

The working electrodes were prepared by sealing small diameter platinum wires in glass and polishing to a planar surface. The electrodes were electrochemically covered with a thin film of mercury by serving as cathodes in a solution of mercuric nitrate in diluted aqueous nitric acid. Reference electrodes were Ag/Ag$^+$ in DMF constructed as described by Moe[26] and stored until the potential was constant. The counter electrodes were platinum wires sealed in glass. The voltammetric cells were cylindrical tubes (50 ml) fitted with a B 29 joint to accomodate a plastic electrode holder equipped with a nitrogen inlet. The volume of the test solutions was 10 ml.

Instrumentation. The potentiostat was a PAR 173/176 driven by a PAR 175 signal generator. Differentiation of linear sweep voltammograms was achieved by application of a PAR 189 selective amplifier in the bandpass mode as earlier destribed.[27] The experimental data were recorded on a Nicolet 2090-3C/206-2 digital oscilloscope interfaced to a Hewlett Packard HP 9826 A desk computer equipped with an HP 2671 G printer and an HP 7475 A plotter. The voltammetric solutions were thermostated by having the cell immersed in water of known temperature kept in a well insulated Dewar flask.

Measurement procedures and precision. Data acquisition by application of differentiated LSV curves has been detailed described elsewhere[27,28] and need not to be repeated here. The direct processing of the voltammograms which is similar to the published procedure was carried out as follows: 1) An equation for the base line was calculated by linear regression of the data points recorded well in front of the rising part of the LSV curve. All the following current data were measured as the distance to the extrapolated base line. 2) The peak point was located by a maximum procedure and the peak current was calculated as the average of the 10 data points closest to the peak point in order to minimize contributions from electrical noise. 3) The peak potential was located by fitting the data points close to the peak point (±15 mV) to a third order polynomial from which the peak potential was found by differentiation. 4) The point closest to $I = \frac{1}{2}I_p$ was located and a linear regression line was evaluated from the data points (±15 mV) close to this crude estimate of $E_{p/2}$. The value of $E_{p/2}$ was finally calculated as the potential at which the distance between the two regression lines was exactly equal to $\frac{1}{2}I_p$. The entire procedure was tested on theoretical data and the error introduced by the fitting procedures was estimated to be less than 0.05 mV. The standard deviation in three repetitive experiments was 0.2 mV for $E_{p/2}$ and 0.3 mV for E_p.

Digital simulation

In dimensionless notation, the equations describing the variation of concentrations, z, with time, τ, and distance from the electrode surface, x, are of the general form

$$\delta z/\delta\tau = \delta^2 z/\delta x^2 + \varkappa \qquad (15)$$

where the second order differential accounts for the diffusion and $\varkappa$ represents a kinetic term which depends on the actual mechanism. Solution of equations like (15) under the boundary conditions given by the electrochemical experiment is conveniently carried out by digital simulation.[29,30] In order to simplify the computational problem, it is common practice to separate the evaluation of the diffusion terms and the kinetic terms and first evaluate an array of intermediate concentration values, z_m, taking only diffusion into account. The values of z_m are then used as input for the evaluation of the kinetic terms. This procedure was also followed in the present work. The diffusion problem was handled by help of the explicit formulation described by Feldberg[29] and the subsequent calculation of the kinetic contributions was carried out by application of the integrated rate laws as originally proposed by Feldberg and Auerbach[31] and later readvocated by Flanagan and Marcoux.[32] The heterogeneous electron transfer was assumed to be Nernstian.

For mechanism I under strictly pseudo first order conditions, the kinetic terms are as follows:

$$\begin{aligned} da/d\tau &= \lambda_3 bc \\ db/d\tau &= -\lambda_2' b - \lambda_3 bc \\ dc/d\tau &= \lambda_2' b - \lambda_3 bc \end{aligned}$$

in which a, b and c represent $[\mathrm{A}]/C_A^\circ$, $[\mathrm{A}^{\cdot-}]/C_A^\circ$ and $[\mathrm{AH}^{\cdot}]/C_A^\circ$, respectively and the dimensionless rate constants, λ_2' and λ_3, are defined as $k_2'RT/(\nu nF)$ and $k_3C_A^\circ RT/(\nu nF)$. By application of the steady state principle on AH$^{\cdot}$ (kinetics only), *i.e.* $dc/d\tau = 0$, the equations are reduced to

$$\begin{aligned} da/d\tau &= \lambda_2' b \\ db/d\tau &= -2\lambda_2' b \end{aligned}$$

or more conveniently by introduction of the artificial species $2a+b$

$$\begin{aligned} \mathrm{d}(2a+b)/\mathrm{d}\tau &= 0 \\ \mathrm{d}b/\mathrm{d}\tau &= -2\lambda_2' b \qquad (16) \end{aligned}$$

Equation (16) is finally integrated in the usual way to give an expression for b.

$$\int_{b_m}^{b} \frac{\mathrm{d}b}{b} = -2\lambda_2' \int_{\tau}^{\tau+\Delta\tau} \mathrm{d}\tau$$

$$\ln \frac{b}{b_m} = -2\lambda_2' \Delta\tau$$

$$b = b_m \exp(-2\lambda_2' \Delta\tau)$$

The differential equations describing the kinetics for mechanism I in general are:

$$\begin{aligned} \mathrm{d}a/\mathrm{d}\tau &= \lambda_3 bc \\ \mathrm{d}b/\mathrm{d}\tau &= -\lambda_2 bd - \lambda_3 bc \\ \mathrm{d}c/\mathrm{d}\tau &= \lambda_2 bd - \lambda_3 bc \\ \mathrm{d}d/\mathrm{d}\tau &= -\lambda_2 bd - \lambda_4 de \\ \mathrm{d}e/\mathrm{d}\tau &= \lambda_3 bc - \lambda_4 de \end{aligned}$$

Where a, b, c and λ_3 have the same significance as before. The parameters d and e represent $[\mathrm{PhOH}]/C_A^\circ$ and $[\mathrm{AH}^-]/C_A^\circ$, respectively and the rate constants λ_2 and λ_4 are given by $\lambda_2 = k_2 C_A^\circ RT/(vnF)$ and $\lambda_4 = k_4 C_A^\circ RT/(vnF)$. If it is assumed in this case that $\mathrm{d}c/\mathrm{d}\tau = \mathrm{d}e/\mathrm{d}\tau = 0$, the mechanism can be described by the following three equations:

$$\begin{aligned} \mathrm{d}(2a+b)/\mathrm{d}\tau &= 0 \\ \mathrm{d}b/\mathrm{d}\tau &= -2\lambda_2 bd \qquad (17) \\ \mathrm{d}d/\mathrm{d}\tau &= -2\lambda_2 bd \end{aligned}$$

Introduction of the stoichiometric condition

$$\begin{aligned} b_m - b &= d_m - d \quad \text{or} \\ d &= d_m - b_m + b \qquad (18) \end{aligned}$$

now allows for the further reduction of (17) to an equation, (19), exclusively in b.

$$\mathrm{d}b/\mathrm{d}\tau = -2\lambda_2 b(d_m - b_m + b) \qquad (19)$$

and thus

$$\int_{b_m}^{b} \frac{\mathrm{d}b}{b(d_m - b_m + b)} = -2\lambda_2 \int_{\tau}^{\tau+\Delta\tau} \mathrm{d}\tau \qquad (20)$$

The left hand side of eqn. (20) is of the general form

$$\int \frac{\mathrm{d}b}{b(\alpha + \beta b)} = \frac{1}{\alpha} \ln \frac{b}{\alpha + \beta b}$$

Which after the appropriate substitution of α and β results in the following expression for b

$$b = \frac{b_m (d_m - b_m)}{d_m \exp(2\lambda_2 \Delta\tau(d_m - b_m)) - b_m}$$

The value of d is finally obtained from eqn. (18).

For mechanism III is analogously obtained

$$\begin{aligned} \mathrm{d}a/\mathrm{d}\tau &= \lambda_3 bc \\ \mathrm{d}b/\mathrm{d}\tau &= -\lambda_2 bd - \lambda_3 bc \\ \mathrm{d}c/\mathrm{d}\tau &= \lambda_2 bd - \lambda_3 bc \\ \mathrm{d}d/\mathrm{d}\tau &= -\lambda_2 bd - \lambda_4 de - \lambda_{14} df \\ \mathrm{d}e/\mathrm{d}\tau &= \lambda_3 bc - \lambda_4 de \\ \mathrm{d}f/\mathrm{d}\tau &= \lambda_2 bd + \lambda_4 de - \lambda_{14} df \end{aligned}$$

in which the additional parameters are defined as: $f = [\mathrm{PhO}-]/C_A^\circ$ and $\lambda_{14} = k_{14} C_A^\circ RT/(vnF)$ and by a procedure similar to that described for mechanism I, this time assuming $\mathrm{d}c/\mathrm{d}\tau = \mathrm{d}e/\mathrm{d}\tau = \mathrm{d}f/\mathrm{d}\tau = 0$, the following equations and expressions are obtained:

$$\begin{aligned} \mathrm{d}(2a+b)/\mathrm{d}\tau &= 0 \\ \mathrm{d}b/\mathrm{d}\tau &= -2\lambda_2 bd \\ \mathrm{d}d/\mathrm{d}\tau &= -4\lambda_2 bd \end{aligned}$$

$$b = \frac{b_m (d_m - 2b_m)}{d_m \exp(2\lambda_2 \Delta\tau(d_m - 2b_m)) - 2b_m}$$

$$d = d_m - 2b_m + 2b$$

Values of E_p, $E_{p/2}$ and i_p were obtained from the theoretical data in a manner similar to that described in the experimental section.

Calculations were carried out in double precision at the Sperry-Univac system belonging to the University of Copenhagen or on an HP 9826 A desk computer. No significant difference could be traced between results obtained from the two different sources for the same simulation parameters. Peak potentials were found to vary by 0.02 mV or less by doubling the number of time steps.

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