

The Application of Linear Sweep Voltammetry for the Determination of Rate Constants in the Range 10^5 – 10^8 $M^{-1}s^{-1}$ for Protonation of Anion Radicals in *N,N*-Dimethylformamide

Merete Folmer Nielsen and Ole Hammerich

Department of General and Organic Chemistry, The H. C. Ørsted Institute, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

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The determination of rate constants for protonation of anion radicals in aprotic solvents is complicated by contributions of unknown magnitude from at least two parallel equilibria, (i) and (ii), in which the proton donor (HB) participates in the formation of hydrogen-bonded complexes. The extent to which these equilibria



affect the accuracy of the measured proton-transfer rate constants in the range 10^5 – 10^8 $M^{-1}s^{-1}$ has been evaluated by linear sweep voltammetry (LSV) for a number of proton donors, including phenol, acetic acid and benzoic acid, in *N,N*-dimethylformamide. The error including the contributions from (i) and (ii) was typically 10–20 %.

The evaluation of protonation rate constants in the range given above by LSV may be affected by interference from background current, probably due to the direct discharge of protons, and/or the rate of the primary heterogeneous charge transfer reaction. It was found that the effects of both were absent or strongly diminished when the measurements were based on the determination of $E_{p/4}$ – E_p under second-order conditions, i.e. at low acid concentration, rather than on the conventional determination of E_p – E^0 under pseudo first-order conditions. The theoretical data necessary for the evaluation of second-order rate constants from measured values of $E_{p/4}$ – E_p are given for $T = 298$ K.

Electrochemical techniques are valuable tools for the study of the kinetic and mechanistic aspects of ion radical reactions,^{1–4} one major advantage being that the ion radicals are generated and the kinetics of their follow-up reactions are monitored during the same experiment. Especially double potential step chronoamperometry (DPSC)^{5,6} and derivative cyclic voltammetry (DCV)^{7–9} have been developed to a high degree of precision, and they are now among the most valuable quantitative techniques, whereas conventional cyclic voltammetry (CV)^{5,6,10} and linear

sweep voltammetry (LSV)^{5,6,10} in general are considered as being less suitable for quantitative work.

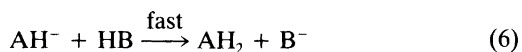
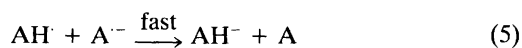
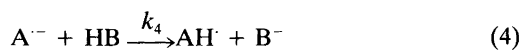
The dynamic ranges of DPSC and DCV depend to some extent on the degree of the material conversion during the experiment. The approximate kinetic windows given by the expressions (1) and (2) are for the most frequently used mode in which the pulse width, τ , (DPSC) or the potential sweep rate, v , (DCV) is adjusted so that the response ratio, R_1 (DPSC) or R'_1 (DCV), is equal to 0.5. The rate constant, k , is that observed for

$$\text{DPSC: } 3 < k/s^{-1} < 300 \quad (1)$$

$$\text{DCV: } 0.3 < k/s^{-1} < 3000 \quad (2)$$

the reaction of the ion radical under first-order or pseudo first-order conditions. The lower limits, corresponding to $\tau \approx 100$ ms and $v \approx 0.1$ Vs⁻¹, are imposed mainly by the requirement that mass transport to and from the working electrode should be restricted to linear diffusion. The upper limits, corresponding to $\tau \approx 1$ ms and $v \approx 1000$ V · s⁻¹, depend on a number of factors, among which are the time constant of the cell, and the quality of the potentiostat and the data sampling equipment. Although CV has been conducted at microelectrodes at sweep rates much higher than 1000 Vs⁻¹ in special cases¹¹⁻¹⁴, it is not a routine procedure to determine rate constants exceeding ~ 3000 s⁻¹ accurately by CV or DCV at the present stage of development of these techniques. However, first-order or pseudo first-order rate constants larger than ~ 3000 s⁻¹ may be determined by LSV.

When the heterogeneous charge transfer is fast (nernstian) and the LSV experiment is carried out under purely kinetic conditions, which means that the rate of the follow-up reaction is fast compared with the sweep rate as evaluated by the magnitude of the parameter $kRT/(vnF)$, k may be determined from measured values of $E_p - E^0$, where E_p is the peak potential of the LSV wave.¹⁵⁻¹⁷ For example, the value of the pseudo first-order rate constant, $k'_4 = k_4 C_{\text{HB}}^0$, associated with the protonation mechanism (3) – (6) and rate law (7) may be estimated from eqn. (8). Here, and in the following, the solution concentration and the stoichiometric concentration of the species X are given as [X] and C_X^0 , respectively. Relationships similar to eqn. (8) exist for other simple rate laws.¹⁵⁻¹⁷

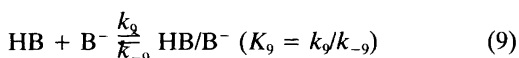


$$d[\text{A}^-]/dt = -2k_4 C_{\text{HB}}^0 [\text{A}^-] = -2k'_4 [\text{A}^-] \quad (7)$$

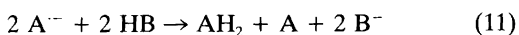
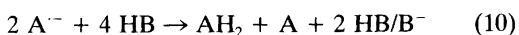
$$E_p - E^0 = -\frac{RT}{nF} \left(0.783 - \frac{1}{2} \ln \frac{k'_4 RT}{2vnF} \right) \quad (8)$$

Values of $E_p - E^0$ may be measured to a precision of ± 1 mV or better by application of modern data sampling techniques,^{9,18-21} and therefore one might expect that k'_4 values of high quality can be obtained as just described. However, the determination of accurate rate constants for rapid proton transfer reactions in aprotic solvents by LSV or any other electrochemical technique is not as straightforward as it may seem from the example given above.

In cases where the follow-up reaction is a second-order process such as (4), it has been observed²² that concentration ratios, $C_{\text{HB}}^0/C_{\text{A}}^0$, in the lower end of the range 5–100 are not sufficiently large to secure the pseudo first-order conditions normally aimed at during kinetic studies. For proton transfer reactions in particular, the deviations from pseudo first-order conditions are accentuated in aprotic solvents by formation of hydrogen-bonded complexes between HB and the corresponding base, B⁻ (eqn. 9).²³⁻²⁷ The values of K_9 fall typically in the region 10²–10⁵ M⁻¹.²³⁻²⁷

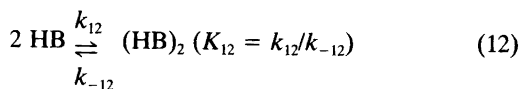


In the limiting case in which k_9 and K_9 are sufficiently large that reaction (9) may be considered as a fast and irreversible process, the stoichiometry of the protonation scheme within the time scale of the voltammetric experiment involves the consumption of four molecules of HB (eqn. 10) instead of two (eqn. 11) for each two molecules



of A⁻ consumed, and, accordingly, the lower limit of $C_{\text{HB}}^0/C_{\text{A}}^0$ at which the deviations from pseudo first-order conditions will be detected is twice that without this additional complication. Such deviations from pseudo first-order conditions may result in peak potential shifts of several mV during LSV,²² and may affect data obtained by CV and DCV as well.^{28,29}

Another parallel reaction which may interfere in the voltammetric determination of rate constants for proton transfer reactions in aprotic solvents is the equilibrium between HB and the corresponding dimer, (HB)₂ (eqn. 12).²⁸ The influence of this reaction is obviously most important



at the higher end of the concentration range $C_{\text{HB}}^0/C_{\text{A}}^0 = 5\text{--}100$. Unfortunately, values of k_{12} and K_{12} have been reported for only a few acids in the solvents most often used in electroanalytical work.³⁰ As an example, K_{12} for benzoic acid in *N,N*-dimethylformamide (DMF) has been estimated^{31,32} to be of the order of 0.15 M^{-1} . This means that the equilibrium concentration of $(\text{PhCOOH})_2$ in a solution nominally 0.1 M in PhCOOH will amount to approximately 1 mM , or in other words, a concentration in the same range as the substrate concentration in a typical voltammetric experiment. The relationship between the acidity constants for HB (K_{HB}) and $(\text{HB})_2$ ($K_{(\text{HB})_2}$) is given by eqn. (13), and since K_9

$$K_{(\text{HB})_2} = K_{\text{HB}}K_9K_{12} \quad (13)$$

in general is several orders of magnitude larger than K_{12} it follows that $K_{(\text{HB})_2} \gg K_{\text{HB}}$; it is therefore clear that the rate constants measured at high values of $C_{\text{HB}}^0/C_{\text{A}}^0$ may reflect kinetic contributions not only from HB, but also from $(\text{HB})_2$.

The influence of the two equilibria, (9) and (12), can be only partially eliminated without the introduction of other kinetic complications. For example, it was observed²⁹ that the presence of Li^+ ions in the voltammetric solution suppresses effectively the formation of PhOH/PhO^- due to complexation of PhO^- by Li^+ ; however, at the same time the proton transfer rate was observed to increase, which was attributed to the participation of Li^+/PhOH complexes in the proton transfer step.

Clearly, the ideal situation would be to be able to include all the proper rate and equilibrium data in the theoretical treatment of the experimental results in order to obtain accurate values of k_4 . However, apart from being an enormous enterprise in digital simulation, the necessary data are normally not available for this approach to be feasible. The question which we will attempt to answer in this paper is then: how accurately is it generally possible to determine rate constants for protonation of anion radicals in aprotic solvents such as DMF by LSV without having access to these data?

The expected effects of reactions (9) and (12) on the observed values of the rate constant k_4 . The kinetic contributions from reactions (9) and (12) depend on the stoichiometric concentration of HB, C_{HB}^0 , and the concentration ratio, $C_{\text{HB}}^0/C_{\text{A}}^0$; let us as a beginning analyze the expected effects of the magnitudes of these two parameters on the experimentally determined values of k_4 in more detail.

The ideal experimental conditions would include (i) high values of $C_{\text{HB}}^0/C_{\text{A}}^0$ in order that the deviations from pseudo first-order conditions should be small and independent of the magnitudes of k_9 and K_9 , and (ii) low values of C_{HB}^0 in order to minimize contributions from $(\text{HB})_2$ as proton donor. However, in practical work it is not possible to comply with these two requirements at the same time. The necessary consequence of a high $C_{\text{HB}}^0/C_{\text{A}}^0$ value and a low C_{HB}^0 value is a low value of C_{A}^0 , but substrate concentrations much less than $1\text{--}2 \text{ mM}$ will, in general, cause detection problems due to low signal-to-noise and signal-to-background ratios. With this additional restriction in mind, a high $C_{\text{HB}}^0/C_{\text{A}}^0$ value will inevitably lead to a high C_{HB}^0 value also. It has been shown²²⁻²⁸ that C_{HB}^0 should be at least $20\text{--}40 \text{ mM}$ at $C_{\text{A}}^0 = 1 \text{ mM}$ if the deviations from pseudo first-order conditions are to be negligible. As an unwanted consequence of this we have to accept the contributions, if any, from $(\text{HB})_2$ as proton donor. Under these experimental conditions, the application of eqn. (8) for the evaluation of k_4' may lead to an *overestimate* of the rate constant due to the enhanced acidity of $(\text{HB})_2$ compared to HB. With the general lack of data for k_{12} , K_{12} and the relative kinetic acidities of HB and $(\text{HB})_2$ in mind, it is impossible to predict the magnitude of this overestimate.

On the other hand, in order to minimize the kinetic contributions from $(\text{HB})_2$ we have to operate at C_{HB}^0 values as small as possible, which due to the restrictions imposed on C_{A}^0 will cause $C_{\text{HB}}^0/C_{\text{A}}^0$ to be small as well. In other words, to avoid the complications arising from participation of $(\text{HB})_2$ we now have to accept the unwanted deviations from pseudo first-order conditions accentuated by equilibrium (9). The result is that the value of the solution concentration of HB, $[\text{HB}]$, will be significantly smaller than C_{HB}^0 , and, accordingly, the application of eqn. (8) in this concentration region will lead to an *underestimate* of k_4' , the extent of which depends on

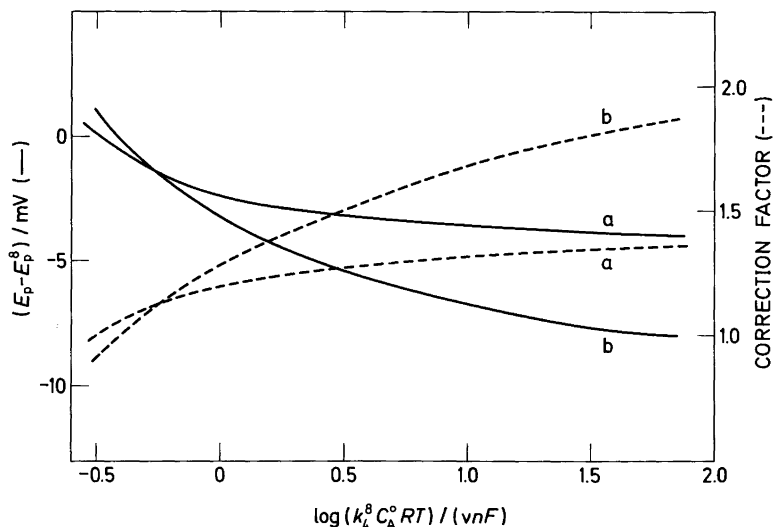


Fig. 1. The effect of deviations from pseudo first-order conditions on the peak potential (full lines) for (a) mechanism (3) – (6) and (b) mechanism (3) – (6) plus fast and irreversible equilibrium (9), and the factor by which rate constants obtained from eqn. (8), k_4^0 , should be corrected to compensate for the deviations (broken lines).

$C_{\text{HB}}^0/C_{\text{A}}^0$ as well as the magnitudes of k_4 , k_9 and K_9 . As an illustration of this effect we have calculated the error in $E_p - E^0$ and in the resulting value of k_4 for (a) mechanism (3) – (6) and (b) the same mechanism including fast and irreversible (9) as a function of $k_4^0 C_{\text{A}}^0 RT / (vnF)$ at $C_{\text{HB}}^0/C_{\text{A}}^0 = 5$, where k_4^0 is the value of k_4 resulting from the application of eqn. (8). The results are shown graphically in Fig. 1, and it is seen that the error in k_4 may easily amount to 25 % or more.

This latter situation can be improved by taking into account in the theoretical treatment of the experimental data that the reaction conditions at low values of $C_{\text{HB}}^0/C_{\text{A}}^0$ are, in fact, second-order and not pseudo first-order. Doing this will allow us to employ concentration ratios much smaller than e.g. 5, and thus further minimize the effect of $(\text{HB})_2$. However, when $C_{\text{HB}}^0/C_{\text{A}}^0$ becomes smaller than approximately 1 for mechanism (3) – (6), or 2 for the same mechanism including the fast and irreversible formation of HB/B^- , the voltammograms no longer exhibit a single peak, but split into two peaks, the first of which may appear as a shoulder on the second. The first peak reflects the formation of A^- followed by reaction with HB , and the second peak is associated with the formation A^- in a reaction layer essentially depleted for HB . The effect, which is

similar to that observed in other second-order cases,³³⁻³⁶ is illustrated in Fig. 2 by simulated voltammograms for mechanism (3) – (6) at $k_4^0 C_{\text{A}}^0 RT / (vnF) = 200$ and with two different values of $C_{\text{HB}}^0/C_{\text{A}}^0$. Obviously, eqn. (8) is no longer valid for the evaluation of k_4 , which instead may be ob-

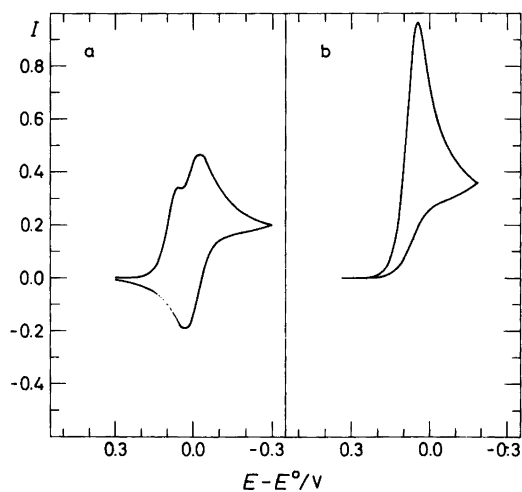


Fig. 2. Simulated voltammograms for mechanism (3) – (6) at $T = 298 \text{ K}$, $k_4^0 C_{\text{A}}^0 RT / (vnF) = 200$, and (a) $C_{\text{HB}}^0/C_{\text{A}}^0 = 0.5$ and (b) $C_{\text{HB}}^0/C_{\text{A}}^0 = 5$.

tained from measurements of e.g. $E_{p/4}-E_p$, where $E_{p/4}$ is the potential at which the current, i , is equal to $i_p/4$. These measurements are discussed in detail in a later section in which the interested reader may also find the theoretical data necessary for determination of k_4 in mechanism (3) – (6) at $C_{\text{HB}}^0/C_A^0 = 0.5$.

Having now taken the second-order nature of the reaction into account, we need only be concerned about the effect of equilibrium (9). If (9) is not of importance under the reaction conditions, and at the same time the theoretical analysis of the experimental data is based on steps (3) – (6) only, the measurements carried out at e.g. $C_{\text{HB}}^0/C_A^0 = 0.5$ will in principle give the correct answer provided no other complications, chemical or instrumental, are encountered. As the effect of equilibrium (9) increases, the value of [HB] will be reduced compared to that in the absence of reaction (9) and, accordingly, protonation takes place at a lower rate, with the result that the observed rate constant will still be an *underestimate* of k_4 .

Results and discussion

Comparison of the k_4 values obtained from two series of measurements, one at e.g. $C_{\text{HB}}^0/C_A^0 = 50$ [which may result in an overestimate of k_4 due to reaction (12)] and another at e.g. $C_{\text{HB}}^0/C_A^0 = 0.5$ [which may result in an underestimate of k_4 due to reaction (9)], will provide us with some insight into the importance of these two parallel reactions. We have therefore determined k_4 for the

protonation of a number of anion radicals derived from aromatic hydrocarbons by a variety of acids in DMF at $C_A^0 = 2$ mM and $C_{\text{HB}}^0 = 1$ and 100 mM, using eqn. (8) for the evaluation of k_4 at $C_{\text{HB}}^0/C_A^0 = 50$ and the method based on measurements of $E_{p/4}-E_p$ at $C_{\text{HB}}^0/C_A^0 = 0.5$.

The resulting values of $k_4(0.5)$ and $k_4(50)$, where the numbers in parentheses refer to the concentration ratios, are summarized in Table 1. However, before going into further discussion of the effects of reactions (9) and (12) on the magnitude of the observed protonation rate constants, we wish to point out a number of experimental problems encountered during the measurements at $C_{\text{HB}}^0/C_A^0 = 50$ and to describe the evaluation of k_4 from measurements of $E_{p/4}-E_p$.

Experimental difficulties and trends in the data at $C_{\text{HB}}^0/C_A^0 = 50$. When A was more difficult to reduce than naphthalene ($E_p = -2.50$ V vs. SCE), or the acid was stronger than benzoic acid, it was generally observed that the data at $C_{\text{HB}}^0 = 100$ mM were of poor quality, or in some cases even impossible to obtain, due to interference of the background current. We suspect the origin of this problem to be discharge of protons, which in the absence of other unwanted effects seems to put a maximum value of 10^6 – 10^7 $\text{M}^{-1}\text{s}^{-1}$ on the protonation rate constants that can be obtained through measurements of E_p-E^0 at the excess concentration of HB necessary for the application of eqn. (8) at comfortable values of C_A^0 . The problem was never encountered during the $E_{p/4}-E_p$ measurements in which C_{HB}^0 was only

Table 1. Rate constants (k_4) determined by LSV for protonation of anion radicals by various acids in DMF. Supporting electrolyte was Bu_4NBF_4 (0.1 M); $C_A^0 = 2$ mM and $T = 298$ K.

Substrate (A)	Acid (HB)	$k_4(0.5)$ / $\text{M}^{-1}\text{s}^{-1}$	$k_4(50)$ / $\text{M}^{-1}\text{s}^{-1}$	$k_4(\text{average})$ / $\text{M}^{-1}\text{s}^{-1}$
Anthracene	<i>p</i> -Chlorophenol	$4.4 \cdot 10^4$	$5.6 \cdot 10^4$	$5.0 \cdot 10^4$
Anthracene	Acetic acid	$9.8 \cdot 10^5$	$9.5 \cdot 10^5$	$9.7 \cdot 10^5$
Anthracene	Benzoic acid	$2.7 \cdot 10^6$	$3.2 \cdot 10^6$	$3.0 \cdot 10^6$
Anthracene	<i>p</i> -Chlorobenzoic acid	$4.8 \cdot 10^6$	– ^a	$(4.8 \cdot 10^6)$
Anthracene	Pentachlorophenol	$6.2 \cdot 10^7$	– ^a	$(6.2 \cdot 10^7)$
Naphthalene	Phenol	$2.8 \cdot 10^5$	$3.3 \cdot 10^5$	$3.1 \cdot 10^5$
2-Methoxy-naphthalene	Phenol	$9.1 \cdot 10^5$	$1.4 \cdot 10^6$	$1.2 \cdot 10^6$
2,3-Dimethoxy-naphthalene	Phenol	$3.2 \cdot 10^6$	$3.5 \cdot 10^6$ ^b	$3.4 \cdot 10^6$

^aNot measurable due to background interference. ^bMinimum value due to heterogeneous charge transfer interference.

equal to 1 mM, and the resulting low value of $C_{\text{HB}}^{\circ}/C_{\text{A}}^{\circ}$, 0.5, caused the acid close to the working electrode to be essentially consumed at the early stages of the voltage sweep before the potential was sufficiently negative for the reduction of protons to become an appreciable problem.

The application of eqn. (8) requires¹⁶ (i) that the voltammetric experiment is conducted under purely kinetic conditions and (ii) that the heterogeneous charge transfer reaction [eqn. (3)] is reversible (nernstian). The first of these requirements translates into expression (14) at a

$$\lambda > 0.83; \lambda = k_{\text{het}}RT/(v_nF) \quad (14)$$

measurement precision of $\pm 2 \text{ mV}^{16}$ (see Experimental). The lowest value of λ related to the present measurements was approximately 14, which refers to the protonation of anthracene anion radical by *p*-chlorophenol at $v = 10 \text{ Vs}^{-1}$, and this value is almost 17 times that required by expression (14). Thus, there seems no doubt that all the reactions included in the study took place under purely kinetic conditions as defined above.

The second requirement, that the heterogeneous charge transfer may be considered as a reversible process, may be expressed as (15)¹⁶ in which k_{het} is the electron transfer rate constant, D is the diffusion coefficient, assumed to be identical for A and A^{-} , and λ has the same meaning as in (14). If k_{het} is not sufficiently large to satisfy expression (15), i.e. the reaction is under mixed kinetic and charge transfer control, the observed

$$\log \Lambda > \frac{1}{4} \log \lambda + 1.24;$$

$$\Lambda = k_{\text{het}}/[DvnF/(RT)]^{\frac{1}{2}} \quad (15)$$

values of $k_4(50)$ will increase with decreasing sweep rate. This behavior was observed in some cases, as illustrated by two of the three data sets given in Table 2. In the first series, for the protonation of anthracene anion radical by *p*-chlorophenol, the values of $k_4(50)$ are essentially independent of the sweep rate. In the second, for the protonation of anthracene anion radical by benzoic acid, the value of $k_4(50)$ starts to decrease at $v \approx 2 \text{ Vs}^{-1}$, and in the third series, for the protonation of 2,3-dimethoxynaphthalene anion radical by phenol, the decreasing trend in $k_4(50)$ is apparent in the entire sweep rate range. At $v = 2 \text{ Vs}^{-1}$, where the trend starts to become apparent in the second series, the observed value of $k_4(50)$ is equal to $3.02 \cdot 10^6 \text{ M}^{-1}\text{s}^{-1}$, and introduction of this value in expression (15) results in a minimum value of 3.9 cm s^{-1} for k_{het} (anthracene). This is close to the value ($4\text{--}5 \text{ cm s}^{-1}$) determined experimentally^{37,38} under conditions similar to those of the present study, or in other words, the trend starts to appear at approximately the expected sweep rate. The same type of analysis carried out for the third series results in a minimum value of 1.9 cm s^{-1} for k_{het} (2,3-dimethoxynaphthalene) at the lowest sweep rate, 0.1 Vs^{-1} , and this minimum value is even higher than the experimental value ($\sim 1 \text{ cm s}^{-1}$) for unsubstituted naphthalene.³⁹ Thus, in this case, expression (15) does not appear to be fulfilled at any sweep rate. Although measurements of k_{het} in the range 1–10

Table 2. The influence of the heterogeneous charge transfer rate on the values of the protonation rate constant, k_4 , calculated from eqn. (8). Supporting electrolyte was Bu_4NBF_4 (0.1 M); $C_{\text{A}}^{\circ} = 2 \text{ mM}$, $C_{\text{HB}}^{\circ} = 100 \text{ mM}$, $T = 298 \text{ K}$.

Sweep rate $/\text{V s}^{-1}$	$k_4(50)/\text{M}^{-1}\text{s}^{-1}$		
	Anthracene <i>p</i> -Chlorophenol	Anthracene Benzoic Acid	2,3-Dimethoxy- naphthalene Phenol
0.1	— ^a	— ^b	$3.52 \cdot 10^6$
0.2	— ^a	— ^b	$2.99 \cdot 10^6$
0.5	$5.88 \cdot 10^4$	$3.11 \cdot 10^6$	$2.00 \cdot 10^6$
1.0	$5.61 \cdot 10^4$	$3.39 \cdot 10^6$	$1.78 \cdot 10^6$
2.0	$5.15 \cdot 10^4$	$3.02 \cdot 10^6$	$1.38 \cdot 10^6$
5.0	$5.82 \cdot 10^4$	$2.35 \cdot 10^6$	$0.88 \cdot 10^6$
10.0	$5.39 \cdot 10^4$	$1.95 \cdot 10^6$	$1.01 \cdot 10^6$

^aExcluded due to poor quality of the experimental data. ^bNot measurable due to background interference.

Table 3. Theoretical values of $E_{p/4}-E_p$ for mechanism (3) – (6) at $C_{HB}^o/C_A^o = 0.5$ and $T = 298$ K.

$\log \left[\frac{k_4 C_{HB}^o RT}{\nu n F} \right]$	$(E_{p/4}-E_p)/mV$
0	80.8
0.176	81.5
0.301	82.5
0.477	84.8
0.699	90.2
0.845	96.0
1.000	103.2
1.176	111.1
1.301	116.3
1.477	123.2
1.699	131.1
1.845	136.1
2.000	141.3
2.176	147.1
2.301	151.2
2.477	156.8
2.699	163.8

cm s⁻¹ are encumbered with large uncertainties³⁷⁻⁴¹, all in all the analysis does support the view that the trends in the data are due to kinetic contributions from the heterogeneous charge transfer reaction. To eliminate, or minimize, this effect on the data, the values given in Table 1 were taken as averages of the results obtained in the sweep rate ranges where no trends could be detected, or (as for protonation of 2,3-dimethoxynaphthalene anion radical by phenol) as the value obtained at the lowest sweep rate in the measurement series.

Evaluation of $k_4(0.5)$ by measurements of $E_{p/4}-E_p$. The shape of the LSV wave is strongly dependent on the magnitude of both the concentration ratio C_{HB}^o/C_A^o and the kinetic parameter $k_4 C_A^o RT/(\nu n F)$ at low values of C_{HB}^o/C_A^o . An example of the dependence on these two parameters has already been given in Fig. 2. In cases where the voltammogram exhibits two well-defined peaks as in Fig. 2a, which for mechanism (3) – (6) at $C_{HB}^o/C_A^o = 0.5$ requires that the value of $k_4 C_A^o RT/(\nu n F)$ is larger than ~ 150 , the peak potential difference may be used for the evaluation of k_4 .^{33,36} However, when $k_4 C_A^o RT/(\nu n F)$ is less than ~ 150 , the pre-peak is reduced to a shoulder on the main peak and another measure of the kinetic shift has to be used to evaluate k_4 .

We have chosen to record the breadth of the LSV wave as reflected by the value of $E_{p/4}-E_p$ for this purpose. This potential difference was found to be more suitable than the analogous difference, $E_{p/2}-E_p$, where $E_{p/2}$ is the potential at which $i = i_p/2$, since the height of the pre-peak or the shoulder is often close to $i_p/2$, and consequently the potential, $E_{p/2}$, will be extremely sensitive to precision in the concentration measurements and the effective stoichiometry of the over-all reaction; for this reason $E_{p/2}$ is not suitable for purely kinetic purposes. Since the basic philosophy behind the measurements presented in this paper was to compare observed values of k_4 under conditions which were predicted to result in either an overestimate or an underestimate of the rate constant arising from the kinetic or stoichiometric contributions of reactions (9) and (12), we have simulated theoretical data for $E_{p/4}-E_p$ at 298 K for mechanism (3) – (6), excluding the possible contributions from the formation of HB/B⁻ complexes [eqn. (9)]. The data are summarized in Table 3, and include potential differences even in the region where the magnitude of $k_4 C_A^o RT/(\nu n F)$ causes the shoulder to separate from the main peak. This allowed us to use the same data acquisition technique in the entire kinetic region of interest.

In a practical experiment, the value of $E_{p/4}-E_p$ was measured at several sweep rates, and $k_4(0.5)$ was obtained by fitting these experimental data to the working curve based on the theoretical data given in Table 3. The fit to the working curve was generally excellent, as demonstrated in Fig. 3 by a data set for the protonation of anthracene anion radical by benzoic acid.

Measurements of $E_{p/4}-E_p$ at $C_{HB}^o/C_A^o = 0.5$ offer a number of experimental advantages compared to measurements of E_p-E^o under attempted pseudo first-order conditions. First, the theoretical treatment incorporates the second-order nature of the reaction as well as the magnitude of the parameter $k_4 C_A^o RT/(\nu n F)$; accordingly, considerations as to whether the reaction takes place under true pseudo first-order conditions and purely kinetic conditions are irrelevant. Second, as already mentioned, the background problem is effectively diminished due to the low values of C_{HB}^o , and third, the correspondingly low effective rate of protonation increases the limit of k_4 at which the rate of the heterogeneous charge transfer process will start to interfere with the determi-

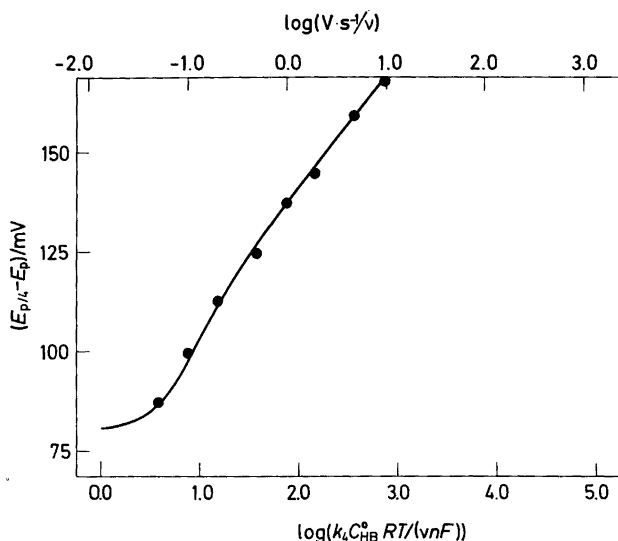


Fig. 3. Theoretical data (full line) for $E_{p/4}-E_p$ at $T = 298$ K for mechanism (3) – (6) at $C_{HB}^0/C_A^0 = 0.5$. The experimental points (●) are for A = anthracene ($C_A^0 = 2$ mM) and HB = PhCOOH ($C_{HB}^0 = 1$ mM), obtained at the sweep rates indicated by the scale at the top of the figure.

nation of k_4 . The latter point is illustrated by the theoretical data given in Table 4, which summarizes values of $E_{p/4}-E_p$ at 298 K and $C_{HB}^0/C_A^0 = 0.5$ as a function of k_4 and k_{het} . The data in Table 4 show that $E_{p/4}-E_p$ is virtually independent of the rate of heterogeneous charge transfer as long as k_{het} is larger than 1 cm s^{-1} . In the range $0.1 < k_{het}/(\text{cm s}^{-1}) < 1$, the values of $E_{p/4}-E_p$ are only significantly affected at the highest sweep rates, which for that reason should not be included in the determination of k_4 .

The effect of equilibria (9) and (12) on the observed k_4 values. A detailed comparison of the

observed $k_4(0.5)$ and $k_4(50)$ values demonstrates that $k_4(50)$ on average is 20% higher than $k_4(0.5)$. This is in keeping with the initial expectations that $k_4(0.5)$ may be underestimated due to the decrease in [HB] caused by the formation of HB/B^- , and that $k_4(50)$ may be overestimated due to the kinetic contributions from $(\text{HB})_2$. However, since the available kinetic data for equilibria (9) and (12) are too scarce to allow the quantitative evaluation of the relative importance of the two processes, we have taken the unweighted average of $k_4(0.5)$ and $k_4(50)$ in Table 1 as the “best” value of k_4 . The deviation from this average amounts in no case to more than $\pm 20\%$,

Table 4. The effect of the rate of the heterogeneous charge transfer process on $E_{p/4}-E_p$ at different values of the proton transfer rate constant, k_4 , at different voltage sweep rates.^a

$k_{het}/$ cm s^{-1}	$k_4/(\text{M}^{-1}\text{s}^{-1})$									
	10^5		10^6			10^7			10^8	
	$v/V \text{ s}^{-1}$		$v/V \text{ s}^{-1}$			$v/V \text{ s}^{-1}$			$v/V \text{ s}^{-1}$	
	0.1	1	0.1	1	10	1	10	100	10	100
∞^b	131.5	90.6	164.1	131.5	90.6	164.1	131.5	90.6	164.1	131.5
10	131.5	90.6	164.1	131.5	90.7	164.1	131.5	90.9	164.0	131.6
1	131.5	90.9	164.0	131.6	91.6	163.7	131.6	94.0	162.9	131.5
0.3	131.6	91.7	163.7	131.6	94.2	162.8	131.5	101.5	160.0	130.9
0.1	131.6	94.0	162.9	131.5	101.0	160.2	131.0	115.5	152.1	129.3

^aValues of $E_{p/4}-E_p$ in mV at 298 K. ^bReversible (nernstian) electron transfer.

and in general the deviation is considerably smaller than that. Thus, our answer to the question raised in the introduction, as to how accurately rate constants for protonation of anion radicals in aprotic solvents like DMF may be determined by LSV, is that the uncertainty, including the unknown contributions from equilibria (9) and (12), typically amounts to 10–20% for k_4 values in the range 10^5 – 10^8 $M^{-1}s^{-1}$, provided interference from the heterogeneous charge transfer process can be avoided experimentally.

The conclusion that the equilibrium between HB, B^- and HB/B^- is only of minor importance for the evaluation of k_4 from E_{p4} - E_p measurements at $C_{HB}^0/C_A^0 = 0.5$ and $C_A^0 = 2$ mM may at first glance seem incompatible with an earlier conclusion^{28,29} that DCV data for the protonation of anthracene anion radical by phenol, obtained under similar conditions ($C_{HB}^0/C_A^0 = 1$ and $C_A^0 = 2$ mM), could be successfully analyzed when equilibrium (9) was incorporated as a fast and irreversible process in the theoretical treatment. The origin of this difference is primarily related to the magnitudes of the k_4 values in the present and the previous study relative to the values of k_9 . In order that equilibrium (9) should behave like a fast and irreversible process, it is required not only that $K_9 \gg 1$, but also that $k_9 \gg k_4$. Considering that k_4 for the reaction between anthracene anion radical and phenol is only $5 \cdot 10^3$ $M^{-1}s^{-1}$ and that k_9 reflects the formation of a hydrogen-bonded complex, which in general is assumed to be a fast reaction, these conditions were without doubt fulfilled during the DCV studies referred to above. However, as the value of k_4 increases, the reactions will inevitably pass into a region in which k_4 and k_9 are of comparable magnitude, and the stoichiometric consequences of equilibrium (9) will gradually lose importance. In the limit, at $k_4 \gg k_9$, the contributions from (9) vanish within the time scale of the experiment, and the reactions will appear to follow mechanism (3) – (6) without interference from (9). In the present study, k_4 is in the range $5 \cdot 10^5$ – $5 \cdot 10^7$ $M^{-1}s^{-1}$, which is between two and four orders of magnitude higher than k_4 for protonation of anthracene anion radical by phenol, and the fact that the analysis of the experimental data shows that equilibrium (9) is only of minor importance in this range of k_4 values indicates that k_9 is in the same region. Values for k_9 in this region may seem small for formation of hydrogen-bonded

complexes, but it should be recalled that HB does not exist as the free acid in aprotic solvents like DMF, but rather as the hydrogen-bonded HB/solvent complex from which HB should be liberated during the formation of HB/B^- .

The data recorded in Table 1 are in fair agreement with the values of k_4 obtained by other techniques in the few cases in which they have been measured. Thus, k_4 for protonation of naphthalene anion radical by phenol has been determined by DPSC at the absolute limit of the capabilities of this technique⁴² to be $1.4 \cdot 10^5$ $M^{-1}s^{-1}$, which should be compared to our average value of $3.1 \cdot 10^5$ $M^{-1}s^{-1}$. The protonation of anthracene anion radical by *p*-chlorophenol has been studied by DCV,⁴³ resulting in a v_3 value of 156 $V s^{-1}$ at $C_{HB}^0/C_A^0 = 10$ and $C_A^0 = 1$ mM corresponding to k_4 equal to $7.8 \cdot 10^4$ $M^{-1}s^{-1}$, as compared to $5.0 \cdot 10^4$ $M^{-1}s^{-1}$ obtained by LSV.

Experimental

The substrates, A, used in this study were anthracene (Prolabo, *pur*), naphthalene (Fluka, *purum*), 2-methoxynaphthalene (Fluka, *purum*) and 2,3-dimethoxynaphthalene (kindly donated by Prof. K. Bechgaard), and the proton donors, HB, were phenol (Ferak), *p*-chlorophenol (Fluka, *purum*; distilled at reduced pressure prior to use), pentachlorophenol (Fluka, *puriss.*), glacial acetic acid (Bie and Berntsen), benzoic acid (Fluka, *purum*; sublimed prior to use) and *p*-chlorobenzoic acid (Fluka, *puriss.*). All compounds were used as received unless otherwise stated.

Solutions of 0.1 M Bu_4NBF_4 ²² in DMF (Ferak; distilled under reduced pressure prior to use) were passed through a column filled with neutral alumina (Woelm, W200) immediately before the substrate and the proton donor were added and the voltammetric measurements were taken.

The electrochemical instrumentation, electrodes, cells and data handling procedures were the same as previously described.²²

Measurements of E_p - E^0 at $C_{HB}^0/C_A^0 = 50$ and $C_A^0 = 2$ mM. Theory predicts that the value of E_p^{rev} for the reversible reduction of a substrate to the anion radical is independent of the voltage sweep rate. However, deviation from this ideal behavior is generally detected when high precision data acquisition instrumentation is used in the experi-

mental determination of E_p^{rev} . The variations in the observed value of E_p^{rev} may amount to ± 1 mV, and it has been proposed¹⁹ that they originate from non-linearity in the amplifiers, which suggested to us that the associated error in the difference, $E_p - E^\circ$, would be minimized if E_p and E° (calculated from E_p^{rev}) were both measured at the same sweep rates. The measurements were carried out as follows: Voltammograms were recorded for each substrate ($C_A^\circ = 2$ mM) before addition of the proton donor at 7 different sweep rates in the interval $0.1\text{--}10$ V s⁻¹, and values of E_p^{rev} and $E_{p/2}^{\text{rev}} - E_p^{\text{rev}}$ were determined at each sweep rate as described earlier.²² The value of E° was then estimated from eqn. (16), in which the final

$$E^\circ = E_p^{\text{rev}} + 0.0285 + (E_{p/2}^{\text{rev}} - E_p^{\text{rev}} - 0.0565)/2 \quad (16)$$

term is a correction for non-ideal behavior. After addition of the proton donor ($C_{\text{HB}}^\circ = 100$ mM), the value of E_p was measured at the same 7 sweep rates and values of the difference, $E_p - E^\circ$, to be used as input for eqn. (8) were calculated. The over all precision of $E_p - E^\circ$ was estimated to be ± 2 mV or better.

Measurements of $E_{p/4} - E_p$ at $C_{\text{HB}}^\circ/C_A^\circ = 0.5$. The measurements were carried out essentially as described earlier.²² The resulting $E_{p/4} - E_p$ values were plotted versus $\log(V \text{ s}^{-1}/\nu)$, and k_4 was obtained by fitting this plot to the working curve as illustrated in Fig. 3. The determination of k_4 in this way included typically $E_{p/4} - E_p$ values obtained at 5–10 different sweep rates.

The experimental values of $E_{p/4} - E_p$ appeared to be only little affected by deviations from the correct amount of positive feedback in the iR -compensation circuit. Typically it was found that a $\pm 10\%$ variation in the iR -setting affected the $E_{p/4} - E_p$ value by 1–3 mV in the sweep rate range $0.1\text{--}10$ V s⁻¹, and the resulting rate constant by less than 10%.

Theoretical data. Digital simulations were carried out using an explicit formulation of the diffusion problem combined with the integrated rate-law for the chemical reaction, as previously described.²² Calculations were performed on an HP 9826A desk computer.

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