The Prepeak Method to Determine Rate Constants of Rapid Reactions following Charge Transfer at Electrodes

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Theoretical data are presented for the determination of second-order rate constants of reactions of electrode-generated intermediates with reactants in limiting concentrations for three common reaction mechanisms. The method is applicable to second-order reactions with rate constants ranging from about $10^6 \ M^{-1} \ s^{-1}$ up to the diffusion-controlled limit. In cases where heterogeneous charge transfer kinetics contribute to the response, calculations must be carried out taking into account the heterogeneous rate constant. The kinetic method is demonstrated using the proton transfer reaction between a radical cation and pyridine, with a rate constant of $2.3 \times 10^8 \ M^{-1} \ s^{-1}$. The method is potentially applicable to a wide range of reactions of electrode-generated intermediates.

Some time ago we reported the use of the potential difference between a prepeak and the main oxidation peak for 9-phenylanthracene (PA) in the presence of limiting amounts of pyridine (N) to determine the rate constant for reaction (1).[1] The observation of a prepeak under

$$PA^{+\bullet} + N \rightarrow PA^{\bullet} - N^{+} \qquad (1)$$

the reaction conditions is a consequence of a rapid chemical reaction between $PA^{+\bullet}$ and pyridine giving rise to a kinetic shift of the current–time curve until pyridine in the reaction layer is essentially consumed. When the latter occurs the voltammetric oxidation of PA resumes in the manner expected in the absence of pyridine. The results of digital simulation of the process which allowed a rate constant to be assigned to reaction (1), were presented.

More recently, we have applied this method to estimate rate constants of several radical cation–nucleophile combination reactions[2–5] as well as that for the reaction between triphenylmethyl radical and oxygen.[6] The method is applicable to the determination of rate constants ranging from about $10^6 \ M^{-1} \ s^{-1}$ up to the diffusion-controlled limit.

Up until now, we have relied upon the Feldberg explicit finite difference digital simulation method,[7] which has been widely used over the past thirty years, to obtain theoretical data from which to derive rate constants. The latter method is not particularly well suited to calculating the voltammetric response of very rapid reactions coupled to charge transfer, and for this reason we have had limited theoretical data available for the prepeak method. Recently, Rudolph[8–10] has developed a very fast implicit finite difference simulation of electrochemical re-

sponses[11–12] which renders the prepeak theoretical data readily available. In this paper we present theoretical data for three different electrode mechanisms which can give rise to prepeaks and show how the method is applied to study the kinetics of very rapid proton transfer reactions of a radical cation.

The prepeak method for determining rate constants of reactions following charge transfer is a modification of the more general method, linear sweep voltammetry, the details of which are well documented.[14]

Results and discussion

In order to apply the prepeak method to determine the rate constant for a reaction of an electrode generated intermediate, the following criteria must be met. (i) The reaction must be sufficiently rapid to give rise to the prepeak behaviour. (ii) In the absence of the limiting reagent, the charge transfer process must give rise to a reversible cyclic voltammogram. (iii) The mechanism, or at least the stoichiometry, of the process must be known.
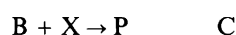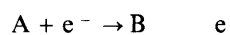
The reason for criterion (i) is obvious while that for other two require clarification. The manner in which the method is used is to measure the potential separation between the two peaks and the potential for the main peak is assumed to be the reversible value which accounts for requirement (ii). Criterion (iii) arises from the fact that several different mechanisms, or stoichiometry, can give rise to the observation of prepeaks under the appropriate conditions.

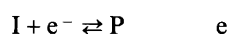Some of the reactions of radical cations with nucleophiles are among the processes which can be studied us-
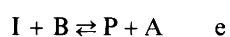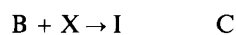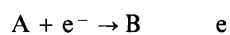
ing the prepeak method. For example, PA (1.0 mM) exhibits a reversible cyclic voltammogram for oxidation to $PA^{+\cdot}$ in acetonitrile–Bu_4NPF_6 (0.1 M) at a voltage sweep rate of 100 mV s^{-1}.[2] The addition of pyridine (0.25 mM) gives rise to a prepeak. The rate constant for the reaction could be assigned by comparing the experimental peak potential difference with that computed by digital simulation.

Electrode mechanisms. The simplest reaction mechanism which can give rise to the observation of a prepeak is the second-order reaction of the electrode-generated intermediate (B) with an added reagent (X) to form the product (P). This is the well known eC mechanism described in Scheme 1.[15] In reactions involving radical ions with electrophiles or nucleophiles the product of the rate determining homogeneous step (C) is a free radical which most frequently undergoes a further electron transfer reaction. The simplest version of the latter is the eCe mechanism. A more commonly observed stoichiometry of this mechanism involves a further rapid reaction (c) of the product of the eCe sequence (P) to give the final product (P'). This is the eCec mechanism which is followed during the reaction of a radical cation with a nucleophile or that of a radical anion with an electrophile.
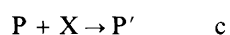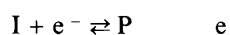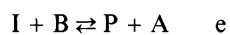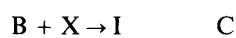
The eC Mechanism

$A + e^- \rightarrow B$ e

$B + X \rightarrow P$ C

The eCe Mechanism

$A + e^- \rightarrow B$ e

$B + X \rightarrow I$ C

$I + B \rightleftarrows P + A$ e

$I + e^- \rightleftarrows P$ e

The eCec Mechanism

$A + e^- \rightarrow B$ e

$B + X \rightarrow I$ C

$I + B \rightleftarrows P + A$ e

$I + e^- \rightleftarrows P$ e

$P + X \rightarrow P'$ c
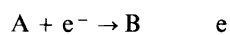
Scheme 1.

Theoretical data. Theoretical prepeak data for the three mechanisms described in Scheme 1 were obtained by digital simulation using the Rudolph method.[16] Data simulated for the three mechanisms with a voltage sweep rate (v) equal to 0.1 V s^{-1}, substrate concentration (C_A) equal to 0.001 M and additional reactant concentration (C_X) equal 0.0005 M are summarized in Table 1. The

Table 1. Differences between prepeak and main peak potentials for the reactions of electrode generated intermediates with limiting reagents.[a,b]

log k/M^{-1} s^{-1}	ΔE^p/mV for mechanism[c]		
	EC	ECE	ECEC
10.0	203	200	223
9.5	188	184	214
9.0	172	170	200
8.5	157	152	183
8.0	141	130	163
7.5	124	110	144
7.0	107	91	126
6.5	88	67	109
6.0	shoulder	shoulder	88

[a] Mechanisms defined in Scheme 1. [b] Conditions: $T=298.15$ K, $v=0.1$ V s^{-1}, $k_s=10^4$ cm s^{-1}, $C_A=0.001$ M, $C_X=0.0005$ M. [c] The polynominal coefficients, c_0, c_1, c_2, c_3, and c_4 for eqn. (2) are: 5.078, 4.260×10^{-3}, 1.696×10^{-4}, -4.230×10^{-7}, 3.571×10^{-10} for EC; 6.029, -1.491×10^{-2}, 4.769×10^{-4}, -2.620×10^{-6}, $5?534\times10^{-9}$ for ECE; 12.830, -2.480×10^{-1}, 2.978×10^{-3}, -1.393×10^{-5}, 2.378×10^{-8} for ECEC.

heterogeneous rate constants (k_s) were assumed to be large (10^4 cm s^{-1}) and the second-order rate constants for all homogeneous reactions other than the rate-determining steps were taken to be equal to 10^{10} M^{-1} s^{-1}. The data show that prepeaks are expected to be observed as long as the second-order rate constant for the electrode-generated intermediate is 10^6 M^{-1} s^{-1} or greater. The data in Table 1 were subjected to a polynomial fitting procedure and a fourth order polynomial, eqn. (2), was observed to give log k accurate to ± 0.01 units.[16]

$$\log(k/\text{M}^{-1}\text{s}^{-1}) = c_0 + c_1\Delta E^p + c_2(\Delta E^p)^2 + c_3(\Delta E^p)^3$$
$$+ c_4(\Delta E^p)^4 \qquad (1)$$

In eqn. (2) ΔE^p is the potential difference in mV between the prepeak and the main peak.

The effect of changing C_A on ΔE^p while holding C_A/C_X constant at 2.0 and k at 10^8 M^{-1} s^{-1} is demonstrated by the data in Table 2. A two-fold change in C_A, keeping all

Table 2. Effect of substrate concentration on prepeak – main peak potential differences.[a,b]

C^A/M	ΔE^p/mV for mechanism		
	EC	ECE	ECEC
0.00025	121	108	141
0.0005	131	119	153
0.001	141	130	163
0.002	151	141	173
0.004	160	152	183

[a] Mechanisms defined in Scheme 1. [b] Conditions: $T=298.15$ K, $v=0.1$ V s^{-1}, $k_s=10^4$ cm s^{-1}, $C_A=0.001$ M, $C_A/C_X=2$, $k=10^8$ M^{-1} s^{-1}.

Table 3. Effect of limiting reagent concentrations on prepeak
— main peak potential differences.[a, b]

| C_X/M | ΔE^P/mV for mechanism | | |
	EC	ECE	ECEC
0.001	151	141	173
0.0008	157	149	178
0.0006	164	157	182
0.0004	173	166	189
0.0003	177	170	192
0.0002	183	177	197
0.0001	192	186	205

[a] Mechanisms defined in Scheme 1. [b] Conditions:
T=298.15 K, v=0.1 V s^{-1}, k_s=10^4 cm s^{-1}, C_A=0.002 M,
k=10^8 M^{-1} s^{-1}.

other parameters constant, results in a 9–10 mV change
in ΔE^P.

The data in Table 3 show the effect of changing C_X
while holding C_A constant at 0.002 M and k at 10^8 M^{-1}
s^{-1}. The other conditions were the same as for the data
in Table 1. The data show that ΔE^P is quite sensitive to
C_X changing as much as 16 mV for a two-fold change in
the variable. This points out the necessity of accurately
knowing C_X. This precaution is sometimes not as trivial
as it may seem, since the added reagent may react with
low concentration impurities in the solvent–electrolyte
system.

The data in Table 4 shows the effect of voltage sweep
rate on prepeak – main peak potential differences for the
three mechanisms. The range of v selected is that com-
monly used in experimental studies. It should be pointed
out that for a simple mechanism where there is only one
kinetic step the change in response due to an increase in
v by a given factor is equivalent to the change in response
due to a decrease in k by the same factor. For example,
the same voltammogram is expected for v = 1.0 V s^{-1} and
k = 10^{10} M^{-1} s^{-1} as would be observed for v = 0.1 V s^{-1}
and k = 10^9 M^{-1} s^{-1}, i.e., k/v remains constant. For the
mechanisms considered here, this relationship is only ex-
pected to hold rigorously for the EC mechanism.

Table 4. Effect of voltage sweep rate on prepeak — main
peak potential differences.[a, b]

| v/V s^{-1} | ΔE^P/mV for mechanism | | |
	EC	ECE	ECEC
0.050	151	141	173
0.100	141	130	163
0.200	131	119	153
0.400	121	108	143
1.000	109	92	128

[a] Mechanisms defined in Scheme 1. [b] Conditions:
T=298.15 K, k_s=10^4 cm s^{-1}, C_A=0.001 M, C_X=
0.0005 M, k=10^8 M^{-1} s^{-1}.

Table 5. Effect of heterogeneous kinetics on prepeak — main
peak potential differences.[a, b]

| k_s/cm s^{-1} | ΔE^P/mV for mechanism | | |
	EC	ECE	ECEC
10^4	203	200	223
5.00	202	199	223
2.00	201	199	222
1.00	200	197	221
0.50	197	194	220
0.20	189	186	214
0.10	175	173	206

[a] Mechanisms defined in Scheme 1. [b] Conditions:
T=298.15 K, C_A=0.001 M, C_X=0.0005 M, v=0.1 V s^{-1},
k=10^{10} M^{-1} s^{-1}.

The data in Tables 1–4 are for conditions where the
heterogeneous rate constants are large and the reactions
at the electrode are diffusion controlled. In practice this
will not always be the case and it is of interest to examine
the effect on the peak potential difference of decreases in
k_s. The effect of k_s will be at a maximum for diffusion-
controlled homogeneous chemical follow-up reactions.
The data in Table 5 are for rate-determining chemical
steps with second-order rate constants equal to 10^{10} M^{-1}
s^{-1}. The values of ΔE^P change by 3 mV or less on a
change in k_s from 10^4 cm s^{-1} to 1 cm s^{-1}. A 3 mV
change in ΔE^P corresponds to about a 20% change in a
rate constant derived using the prepeak method. This
would generally be considered to be an acceptable maxi-
mum error in rate constants of very rapid reactions. How-
ever, at k_s less than 1 cm s^{-1}, a much greater effect of
heterogeneous kinetics is observed. Under these condi-
tions the method could still be used to determine homo-
geneous rate constants but the magnitude of k_s must be
known and appropriate theoretical data must be applied
in the analysis.

Relative diffusion coefficients (D_X/D_A) of additional re-
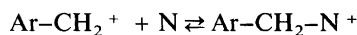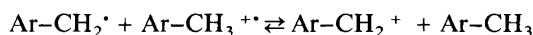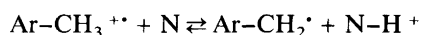actant (X) and substrate (A) also affect ΔE^P. This ratio

Table 6. Effect of diffusion coefficient ratios on differences
between main peak and prepeak potentials.[a, b]

D_X/D_A [c]	ΔE^P/mV	I_p/I_m [d]
0.25	188	0.32
0.50	175	0.45
0.75	169	0.56
1.00	163	0.64
1.50	155	0.78
2.00	149	0.90
3.00	139	1.09
4.00	136	1.24

[a] Data calculated for the ECEC mechanism (Scheme 1).
[b] Conditions: T=298.15 K, v=0.1 V s^{-1}, k_s=10^4 cm s^{-1},
C_A=0.001 M, C_X=0.0005 M. [c] Ratio of diffusion coeffi-
cients of additional reactant (X) to that of substrate (A).
[d] Ratio of current at the prepeak to that at the main peak.

was taken to be unity for the calculation of the data in Tables 1–5. The data in Table 6 were obtained from simulations where D_X/D_A was varied from 0.25 to 4.00 holding all other parameters constant for the ECEC mechanism. The data reveal that both ΔE^P and the ratio of current at the prepeak and main peak (I_p/I_m) depend on D_X/D_A. Since I_p/I_m is strongly dependent on D_X/D_A, the measurement of the current ratio and including this in the simulations eliminates variations in D_X/D_A as a source of significant error in the rate constant determination. If the latter is not taken into account, variations in D_X/D_A in the range shown in Table 6 would result in errors of ± 0.5 in log k.

An experimental prepeak study. The proton transfer reaction between 9-methyl-10-nitroanthracene $(Ar–CH_3)$ radical cation and pyridine (N) in $CH_3CN–Bu_4NPF_6$ (0.1 M) at 298 K was selected as a rapid reaction with which to demonstrate the use of the prepeak method to determine a rate constant.[18] The reaction follows the eCec mechanism as outlined in Scheme 2.

$$Ar–CH_3 \rightleftarrows ArCH_3{}^{+\cdot} + e^-$$

$$Ar–CH_3{}^{+\cdot} + N \rightleftarrows Ar–CH_2{}^{\cdot} + N–H^+$$

$$Ar–CH_2{}^{\cdot} + Ar–CH_3{}^{+\cdot} \rightleftarrows Ar–CH_2{}^+ + Ar–CH_3$$

$$Ar–CH_2{}^{\cdot} \rightleftarrows ArCH_2{}^+ + e^-$$

$$Ar–CH_2{}^+ + N \rightleftarrows Ar–CH_2–N^+$$

Scheme 2.

The voltammogram in the Fig. 1 shows the response observed at a voltage sweep rate of 0.1 V s^{-1} during the oxidation of $Ar–CH_3$ (1.0 mM) in the presence of pyridine (0.5 mM). The difference in potential between the prepeak and the main peak was observed to be equal to 188 mV under these conditions. The peak height ratio (I_p/I_m) equal to 0.45 indicates that D_X/D_A is equal to 0.5. Two series of experiments were carried out in order to evaluate the rate constant for the reaction under these conditions. The data in Table 7 shows the effect of varying the pyridine concentration at a constant $Ar–CH_3$ concentration. Variation of the voltage sweep rate holding reactant concentrations constant gave rise to the data in Table 8. On the basis of these data we assign a rate constant of 2.3×10^8 M^{-1} s^{-1} for the proton transfer reaction.

An analysis of previously reported prepeak data. Owing to difficulties encountered using the explicit finite difference simulation of current time curves under conditions where prepeaks are observed, many of the previously reported data[2] were derived from simulations which covered only
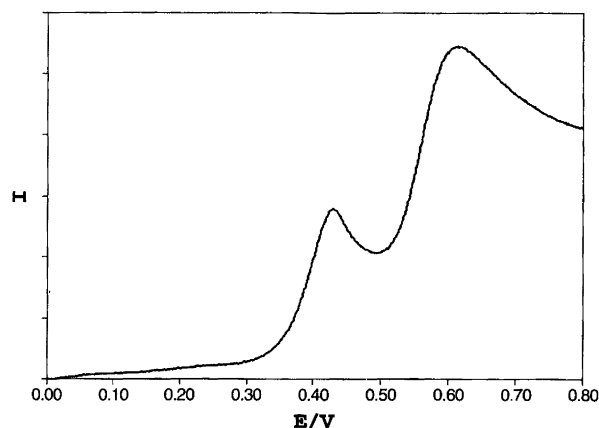

Fig. 1. Linear sweep voltammogram for the oxidation of 9-methyl-10-nitroanthracene (1.0 mM) in the presence of pyridine (0.5 mM) in MeCN–Bu$_4$NPF$_6$ (0.1 M) at a voltage sweep rate of 0.1 V s^{-1}. The potential scale refers to Ag$^+$/Ag in acetonitrile.

Table 7. Variation of the pyridine concentration during a prepeak kinetic study of the reaction between 9-methyl-10-nitroanthracene radical cation and pyridine in acetonitrile.[a]

[Pyridine]mM	ΔE^P/mV	log$(k/M^{-1}\,s^{-1})$[b]
0.2	225	8.4
0.4	211	8.3
0.6	201	8.2
0.8	195	8.2
1.0	190	8.2

[a] Measurements at 298 K using a platinum electrode at a voltage sweep rate of 0.1 V s^{-1} with a substrate concentration equal to 2.0 mM in $CH_3CN–Bu_4NPF_6$ (0.1 M). [b] Obtained by comparison with theoretical data with D_X/D_A equal to 0.50.

Table 8. Variation of the voltage sweep rate during a prepeak kinetic study of the reaction between 9-methyl-10-nitroanthracene radical cation and pyridine in acetonitrile.[a]

Voltage sweep rate/V s^{-1}	ΔE^P/mV	log$(k/M^{-1}\,s^{-1})$[b]
0.05	194	8.3
0.10	188	8.4
0.20	180	8.4
0.40	167	8.3
1.00	151	8.2

[a] Measurements at 298 K using a platinum electrode with a substrate concentration equal to 1.0 mM in the presence of pyridine (0.5 mM) in $CH_3CN–Bu_4NPF_6$ (0.1 M). [b] Obtained by comparison with theoretical data with D_X/D_A equal to 0.50.

the potential region of the prepeak but not the main peak. In deriving rate constants from these data, it was assumed that the potential of the main peak was unaffected by the occurrence of the chemical reaction which gives rise to the prepeak. The simulations that we have carried

Table 9. Prepeak and main peak potential differences used to assign rate constants for the reaction of 9-phenylanthracene radical cation with 4-methylpyridine.

$10^{-7} k/M^{-1} s^{-1}$ [a]	$v/V s^{-1}$ [b]	ΔE^P (observed) [c]	ΔE^P (calc.) [d]
4.63	0.1	161.9	162
4.32	0.2	151.0	150
3.70	0.4	138.5	138
3.82	0.1	159.2	158
4.11	0.2	150.3	150
3.63	0.4	138.2	137
3.82	0.1	159.0	158
4.11	0.2	150.3	150
3.77	0.4	138.8	138

[a] Rate constant assigned in Ref. 2. [b] Voltage sweep rate used in Ref. 2. [c] Peak potential difference at 298 K from Ref. 2. [d] Theoretical peak potential separations calculated from the assigned rate constant using DigiSim.

out using the Rudolph[8-13] method show that there are small potential shifts of the main peak from the reversible value. In order to determine the magnitude of error associated with the neglect of the potential shift of the main peak, the rate constants reported in Ref. 2 were used to calculate ΔE^P and these are then compared with the experimental values in Table 9. The data show there is a maximum of 1 mV difference between the experimental and calculated ΔE^P. We conclude on the basis of this comparison that the error in rate constants[2] which can be associated with the quality of the theoretical data used is negligible.

Preliminary results of a comparison of rate constants of radical cation–nucleophile combination reactions derived using the prepeak method with those obtained in laser flash photolysis studies show a very close correspondence between rate constants derived by the two methods.[19]

Conclusions. Providing that the process is suitable for study by the prepeak method, as outlined in the above discussion, rate constants of homogeneous reactions of electrode-generated intermediates ranging from about 10^6 to 10^{10} $M^{-1} s^{-1}$ can be determined. The results reported here indicate that for reactions involving many aromatic substrates, heterogeneous kinetics will not interfere even for reactions at the diffusion-controlled limit. However, it is necessary to either know or be able reliably to estimate the heterogeneous rate constants for the process in question. The prepeak method is potentially applicable on a wide variety of reactions of electrode-generated intermediates.

Experimental

Linear sweep voltammetry was performed at a planar 0.8 mm platinum electrode using a PAR Model 173D potentiostat driven by a Hewlett-Packard 3314A function generator. The signals were filtered using a Stanford Research System, Inc., Model SR640 dual channel low pass filter before being recorded on a Nicolet Model 310 digital oscilloscope. An IBM AT compatible personal computer was used to control the oscilloscope and the function generator via an IEEE interface. The current–potential curves were collected and averaged at trigger intervals selected to reduce periodic noise.[20] The averaged signals were then treated with a digital frequency domain low pass filter before numerical differentiation. Peak potentials were obtained from the smoothed signal both before and after differentiation. The two methods give comparable precision.[2]

9-Methyl-10-nitroanthracene was prepared by treating (dropwise) a suspension of 9-methylanthracene (3.85 g) in acetic acid (25 ml)/conc. HCl (10 ml) with conc. nitric acid (1.5 ml). After 2 h of vigorous stirring at room temperature the mixture was treated with a 10% aqueous solution of NaOH. The product was isolated in low yield after being passed through a silica gel column. No attempts were made to optimize the synthesis.

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15. The commonly accepted symbolism, e = an electron transfer (either at the electrode or in a homogeneous reaction) and c = a homogeneous chemical reaction, is used in the scheme. Lower case letters are for fast reactions and the upper case letter is for the rate-determining step.
16. Calculations were carried out either using a program written by Dr. M. F. Nielsen of the University of Copenhagen or the commercially available[13] program. Identical results were obtained with the two programs.

17. The coefficients for the polynomial equations are available upon request.
18. Details of these and other radical cation proton transfer reactions will be published later.
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