Electrode Reaction Activation Energies, Reaction Orders, Kinetic Isotope Effects, and Intermediate Life-times without Resort to Calculations

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A general method is developed for the determination of apparent activation energies, reaction orders, and kinetic isotope effects of reactions of electrode generates intermediates. The method is based on equations (i) and (ii). Transient technique observables are functions of time dependent variables such

$$\text{Observable} = f(k_{app} \cdot \text{Variable}) \qquad (i)$$

$$k_{app} = f(C_s C_x TI) \qquad (ii)$$

as voltage sweep rate or pulse width and the apparent rate constant (k_{app}) of the reaction. The latter can be a function of the substrate concentration (C_s), an additional reactant concentration (C_x), the isotopic content (I) of the substrate or reactant and the temperature (T). The value of the observable is first determined under a particular set of conditions and a single factor, depending on which kinetic parameter is being studied, is changed and the variable is then fine-tuned so that the observable remains unchanged. The relative magnitudes of the variable under the two (or more) sets of conditions are then simply related to the relative rate constants.

It has recently been pointed out that the apparent activation energies for reactions of intermediates produced at electrodes can be determined simply and precisely without the explicit knowledge of the rate constants.[1] The latter emerges from the fact that the electrode response to a transient perturbation can be described by (1) where the response (Observable) is related to the perturbation (Variable)

$$\text{Observable} = f(k_{app} \cdot \text{Variable}) \qquad (1)$$

and the apparent rate constant (k_{app}). The method was applied using derivative cyclic voltammetry (DCV)[2] where the observable is the ratio of the derivative of the currents on the backward and forward scans ($R_I' = I_b'/I_f'^P$), and the time-dependent variable is the voltage sweep rate (v) and the appropriate relationship is described by eqn. (2).[1] It was shown that if R_I' is held constant while changing the temperature by fine-tuning v, that the apparent activation energy is given by (3) where c is a constant.[1]

$$R_I' = f(k_{app}/v) \qquad (2)$$

$$\ln v = (-E_a/R)(1/T) + c \qquad (3)$$

In this paper, a general method is developed for examining the mechanisms of electrode reactions. The method is based on eqn. (1) and the previous work is generalized to include reaction orders and kinetic isotope effects. Since the desired relationships are obtained directly from experimental parameters, theoretical calculations or working curves are not necessary. The latter not only makes mechanism analysis possible when the kinetic-diffusion problem cannot be solved theoretically but also eliminates any error associated with approximations necessary in the theoretical treatment.

RESULTS AND DISCUSSION

The kinetics of reactions of intermediates generated at electrodes can be studied by transient techniques and rate constants are normally deter-

mined from relationships based on eqn. (1). For reactions of intermediate B generated at the electrode from A (eqn. 4) theoretical calculations can be

$$A \pm e^- \rightleftarrows B \qquad (4)$$

carried out to give the response as a function of rate constant, substrate concentration, and V according to eqn. (5). In (5) z is 0 for a first order reaction

$$\text{Observable} = f(kC_A^z/V) \qquad (5)$$

$$a = nFv/RT \qquad (6)$$

of B and -1 for a second order reaction. The time-dependent variable V depends on the particular technique and is a, defined as in eqn. (6) for cyclic voltammetry and τ^{-1}, the reciprocal of the pulse width, for potential step methods. The calculations are normally used in the form of a theoretical working curve where the observable is plotted as the ordinate $vs.$ kC_A^z/V.[3] It is generally not possible to solve the kinetic-diffusion problem analytically for cases other than the most simple mechanisms and it is necessary to resort to numerical methods.[4] The most versatile calculation technique is digital simulation.[5]

It was pointed out earlier[1] that it is generally not possible to obtain numerical solutions for the electrode response for complicated mechanisms without making assumptions regarding the relative importance of some of the reaction steps. For example, the disproportionation mechanism where B is generated in (4) and reacts according to (7) and (8) with rate law (9) derived by the steady state assumption, must be treated as two limiting cases depending on the relative importance of the two

$$2B \underset{k_{-7}}{\overset{k_7}{\rightleftarrows}} C + A \qquad (7)$$

$$C \overset{k_8}{\rightarrow} \text{products} \qquad (8)$$

$$-dC_B/dt = 2 k_7 k_8 C_B^2/(k_{-7}C_A + k_8) \qquad (9)$$

terms in the denominator. As the mechanisms get more and more complex, the nature of the assumptions necessary can result in working curves which have little relationship to the actual mechanism of the reaction being considered. An approach has been described whereby the working curves are used to find the general form of the mechanism and then

a concentration dependent rate constant, "k_{obs}" is defined, which in the case of the disproportionation mechanism is given by eqn. (10).[6] This approximate method then allows mechanistic conclusions to be

$$\text{"}k_{obs}\text{"} = 2k_7 k_8/(k_{-7}C_A + k_8) \qquad (10)$$

drawn even in cases where it is not possible to calculate the theoretical response for the mechanism being considered.

To illustrate the difficulties encountered in solving the kinetic-diffusion problem for complex mechanisms it suffices to point out that only recently[7] have attempts to fit two experimental parameters to digitally simulated working curves met with success. The system described involved a relatively simple case, a second order equilibrium (11) followed by first order product forming reactions (12).

$$2 B^{\cdot -} \overset{K_{11}}{\rightleftarrows} B^- - B^- \qquad (11)$$

$$B^- - B^- \overset{k_{12}}{\rightarrow} \text{products} \qquad (12)$$

Since severe approximations are necessary to obtain the theoretical response for most complex mechanisms and even then it may not be possible to obtain satisfactory solutions of the kinetic-diffusion problem for multi-step processes, an approach which does not rely on calculations at all is very attractive. In the following paragraphs, such a method of treating electrode mechanisms is developed.

Kinetic information pertaining to reaction mechanisms. The rate constants that can possibly be obtained using transient electrochemical techniques can be related to microscopic rate constants only in very simple cases. Thus, kinetic data is capable of describing mechanisms only in a semi-quantitative way. However, mechanism analysis does not require microscopic rate constants for each step in the reaction and a reasonably complete overall picture can be obtained if the following data are available:

(i) Reaction orders.
a. With respect to substrate.
b. With respect to additional reactants.
(ii) Temperature effect or apparent activation energies.
(iii) Kinetic isotope effects for isotopically substituted substrate or other reactant.
(iv) The overall rate of the reaction or the lifetime of the electrode generated intermediate.

As in any other mechanism study, other data such as that pertaining to structure-reactivity relationships are desirable when applicable.

Mechanistic evidence in the four categories listed above is generally obtained from evaluation of rate constants measured under various conditions. If rate constants are not accessible, it is usually not possible to conduct a mechanism analysis.* However, it is possible to use the same approach as previously employed for activation energy determinations [1] to obtain evidence in all four categories.

General approach. Eqn. (1) can be applied to derivative cyclic voltammetry and double potential step chronoamperometry (DPSC) by way of eqns. (2) and (13), respectively, where τ refers to the pulse width and R_I is the ratio of the current at 2τ and τ

$$R_I = f(k_{app}\tau) \tag{13}$$

normalized to the no reaction case by dividing by $(1 - 2^{-\frac{1}{2}})$. Experimentally, the ratio, R_I' or R_I, is first adjusted to a convenient value for measurement under the initial conditions by appropriate adjustments in the variable, v or τ. The condition relating to the category of evidence being studied; temperature, substrate or reactant concentration, or isotopic content of the substrate or reactant, is then changed and the variable is fine-tuned so that the observable retains precisely the same value. A series of several such changes then gives k_{app} as a function of the condition being changed. Further details are given under the individual categories.

Reactions orders of electrode processes. Reaction orders of electrode processes have previously been discussed by Bezilla and Maloy [7] following the definition of King.[9] Since the measurement procedure suggested here is designed to directly give the dependence of k_{app} on the quantity being studied, we must use a slightly different definition (14) where

$$R_{A/B} = 1 + z, \ (k_{app}/C_A^Z = constant) \tag{14}$$

A refers to the substrate and B to the electrode generated intermediate as in eqn. (4). It is necessary to consider the possibility that the reaction order observed could reflect the contribution of B (this will always be the case) or a combination of B and A. Mechanisms such as the simple EC would give a reaction order of 1 while that for the EC(dim) mechanism would be 2. The disproportionation

mechanism in the limiting case where $k_{-7}C_A \gg k_8$ (eqn. 9) would then give a reaction order of 1 or when $k_8 \gg k_{-7}C_A$ a value of 2 would be obtained.

When an additional reactant is involved, the reaction order is defined as in (15). In this case the quantity is unambiguous since the order is affected

$$R_X = z, \ (k_{app}/C_X^Z = constant) \tag{15}$$

by a single species.

In either case the reaction order in question can be obtained from the experimentally derived slope (16) where V_c is the value of the variable necessary to hold the observable at the same value at each

$$\text{Reaction order} = f(z), \ (V_c/C_{(A \text{ or } X)}^Z = constant) \tag{16}$$

concentration of A or X. Once the reaction order $(R_{A/B})$ is determined, possible mechanisms can be examined with the associated reaction orders R_A and R_B. For example, an experimental value of $R_{A/B}$ equal to 1.0 could be resolved into $R_B = 2$ and $R_A = -1.0$ or $R_B = 1.0$ and $R_A = 0$. Thus, the reaction order is a very powerful aid to mechanism analysis.

Apparent activation energies of electrode processes. The relationship for DCV has already been described [1] and is illustrated by eqns. (2) and (3). From (13) it is apparent that if the product of k_{app} and τ is to remain constant as the former is increasing τ must be correspondingly decreased. Thus, the activation energy equation relating to DPSC is given by (17) where τ_c is the value of the pulse width necessary

$$\ln (1/\tau_c) = (-E_a/R) (1/T) + c \tag{17}$$

to hold the current ratio R_I constant as the reaction temperature is increased. Once again, the desired information is obtained directly from experimental quantities without using any theoretical relationships to convert the data to rate constants.

Kinetic isotope effects of electrode processes. The isotopic substitution may either be in the substrate or in another reactant and we will consider for simplicity only deuterium kinetic isotope effects. In this case the quantity of interest is $(k_{app})_H/(k_{app})_D$ where the subscripts could refer to isotopic labelling either in the substrate or the other reactant which ever is applicable. The kinetic isotope effect can then be obtained directly from (18) and (19) for

$$(k_{app})_H/(k_{app})_D = (v_c)_H/(v_c)_D \tag{18}$$

$$(k_{app})_H/(k_{app})_D = (\tau_c)_D/(\tau_c)_H \tag{19}$$

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*An exception should be noted here, linear sweep voltammetry (LSV) mechanism analysis [8] does not require evaluation of rate constants.

DCV and DPSC, respectively. Once again, the quantity of interest can be obtained directly from the ratio of the variable magnitudes necessary to hold the respective current ratios constant while the reaction conditions are changed.

Kinetic isotope effects can also be determined directly from LSV data without the need to know the rate constants. Since there do not appear to be any reports of this in the literature, the method will be briefly outlined here. If the substrate is the site of the isotopic labelling, it is necessary first to determine $dE^P/d \log v$, the sweep rate dependence. This then provides one with the change in peak potential for an order of magnitude change in the apparent rate constant. The change in E^P (ΔE^P_1) brought about by the change in isotopes is then determined and the kinetic isotope effect can be calculated from eqn. (20). Likewise, when the site of the isotopic substitution is in another reactant the

$$\log (k_{app})_H/(k_{app})_D = \Delta E^P_1/(dE^P/d \log v) \qquad (20)$$

relationship is similar with $dE^P/d \log C_X$ being substituted for the sweep rate dependence.

The life-time of electrode generated intermediates. Since the proposed method will be most useful in cases where the mechanism is not known and it is not possible to calculate the response for the complex possibilities, the rate constants are inaccessible. However we can relate two quantities, v_1 and τ_1, the variable magnitudes when the corresponding current ratios, R'_I and R_I, are equal to 0.500 to the the homogeneous half-lives of the electrode generated intermediates. We recall that in terms of rate constants the half-lives (t_1) for reactants undergoing first and second order reactions are described by eqns. (21) and (22), respectively. The theoretical data in Table

$$t_1 = (\ln 2)/k \text{ (first order)} \qquad (21)$$

$$t_1 = 1/k \, C_B \text{ (second order)} \qquad (22)$$

1 for three common but significantly different mechanisms show that both τ_1 and v_1 differ from one mechanism to the next.

In order to have a means of determining t_1 for cases with unknown mechanisms the most simple process, the EC mechanism (eqns. 4, 23) was taken as the standard. For this mechanism τ_1 and $(v_1)^{-1}$

$$B \xrightarrow{k} \text{products} \qquad (23)$$

can be normalized to t_1 by multiplying by 1.67 and 0.228 V, respectively. The ECE_h mechanism[8] (eqns. 4, 24–26) differs from the EC by the overall number of electrons transfered per molecule of substrate. Thus, we might expect some function containing

$$B \xrightarrow{k} C \qquad (24)$$

$$C + B \rightleftarrows D + A \qquad (25)$$

$$D \rightarrow \text{products} \qquad (26)$$
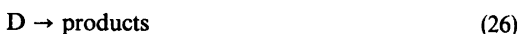
$(n_e)_f$, the number of electrons involved in the forward process, to serve as a normalizing factor for this mechanism. The factor giving the best results for both DPSC and DCV was found to be $(n_e)^{\frac{1}{2}}_f$ (Table 1). The EC(dim) mechanism (eqns. 4, 27) differs from the EC mechanism in that the apparent

$$2 B \xrightarrow{k} \text{products} \qquad (27)$$

reaction order with respect to substrate ($R_{A/B}$) is equal to 2 in this case. The normalizing factor found to be most satisfactory for τ_1 was $(R_{A/B})^{\frac{1}{2}}$. The

Table 1. Half-lives of electrode generated intermediates.

Mechanism	t_1/ms^a	τ_1/ms^b	$(t_1)_\tau/ms^c$	$v_1/Vs^{-1\,d}$	$(t_1)_v/ms^e$	k
EC	1.00	0.60	1.00	228	1.00	$3.04\,v_1{}^f$
ECE_h	1.00	0.40	0.95	161	1.00	$4.31\,v_1{}^f$
EC(dim)^g	1.00	0.86	1.02	219	1.04	$4.57\,v_1 C_A^{-1}$
			0.99(4)		1.01(2)	

^{a} The half-life of the electrode generated intermediate arbitrarily taken to be 1 ms. ^{b} Calculated from theoretical data pertaining to the particular mechanism at 298 K for $R_I = 0.500$. ^{c} Calculated from $(t_1)_\tau = 1.67(n_e)_f^{\frac{1}{2}} \tau_1/(R_B)^{\frac{1}{2}}$ as discussed in the text. ^{d} As in b for the case where $R'_I = 0.500$. ^{e} Calculated from $(t_1)_v = 0.228/v_1 (n_e)_f^{\frac{1}{2}}$ as discussed in the text. ^{f} First order rate constant in s^{-1}. ^{g} For the second order mechanism, t_1 refers to $(kC_B^o)^{-1}$ where C_B^o is the initial concentration of the intermediate. C_B^o was taken to be 10^{-3} M. The rate constant is in M^{-1} s^{-1}.

normalizing factor for $v_{\frac{1}{2}}$ was independent of $R_{A/B}$. Using the appropriate normalizing factors for the three mechanisms resulted in average values of 0.99 and 1.01 ms for the calculated $t_{\frac{1}{2}}$, very close to the theoretical calue of 1.00 ms with standard deviations of ± 0.04 and ± 0.02 for DPSC and DCV, respectively.

The mechanisms listed in Table 1 give $R_{A/B}$ values which reflect only the contribution of R_B (i.e. $R_A = 0$). When this is not the case, it is likely that the normalization procedure will not give such precise estimates of the intermediate lifetimes. However, of the four categories of mechanistic information this one is the least critical. The estimated lifetime will give a measure of the reactivity but since a number of rate constants will generally contribute to the overall rate and the individual contributions will not be separable, having an exact estimate of k_{obs} does not contribute much to the mechanism analysis. For these reasons it would seem that a good estimate is all that is necessary.

CONCLUSIONS

This discussion has shown that it is possible to study complex reaction mechanisms of electrode generated intermediates without the necessity of being able to obtain numerical theoretical data for the mechanisms. This is obviously of great advantage when mechanisms involve several steps and rate constants. The method also provides a reliable estimate of the half-life of the primary intermediate which can be used to estimate the overall rate constant of a reaction.

REFERENCES

1. Parker, V. D. Acta Chem. Scand. B 35 (1981) 51.
2. Ahlberg, E. and Parker, V. D. Acta Chem. Scand. B 33 (1979) 696; J. Electroanal. Chem. 121 (1981) 73.
3. MacDonald, D. D. Transient Techniques in Electrochemistry, Plenum, New York 1977.
4. Nicholson, R. S. and Shain, I Anal. Chem. 36 (1964) 706.
5. Feldberg, S. W. Electroanal. Chem. 3 (1969) 199.
6. Parker, V. D. Acta Chem. Scand. B 35 (1981) 123.
7. Bezilla, B. M., Jr. and Maloy, J. T. J. Electrochem. Soc. 126 (1979) 579.
8. Parker, V. D. Acta Chem. Scand. B 34 (1980) 359 and references therein.
9. King, E. L. J. Chem. Educ. 51 (1974) 186.