Acta Chemica Scandinavica B 38 (1984) 243–248

Electrode Mechanism Analysis by Linear Sweep Voltammetry. V.* The Reaction Order Approach Applied to Competing and Complex Mechanisms

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The rate laws for competing and complex mechanisms of reactions of electrode generated intermediates can be derived directly from plots of the linear sweep voltammetry peak potential *vs.* substrate (A) concentration for experiments conducted at a given sweep rate. For example, a plot of $(3F/RT)E^p$ *vs.* $\ln C_A$ for a mechanism consisting of competitive first and second order reactions of the primary intermediate (B) has two limiting cases at the extremes of C_A. At low C_A the plot is linear with 0 slope while at high C_A the plot is again linear but with unit slope. In the intermediate concentration range the plot is curved upward. The curvature in these plots along with reaction order data obtained by linear sweep voltammetry measurements are sufficient to describe the rate law for the process. Rate constants can be evaluated from theoretical data for the two limiting cases along with the experimentally determined value of C_A where the reaction order in B is half that for the two limiting cases. The entire analysis can be carried out without the necessity of knowing the reversible potential for the charge transfer process.

In an earlier paper in this series[3] it was shown that the rate laws for reactions of intermediate B generated from substrate A in charge transfer reaction (1) can be derived directly from

$$A \pm e^- \rightleftarrows B \qquad (1)$$

experimental linear sweep voltammetry (LSV) peak potentials (E^p) as a function of voltage sweep rate (v), substrate concentration (C_A) and the concentration of any additional reactant (X) that may be involved in the reaction. Rearrangement of the linear equations presented[3] gives eqns. (2) – (4) for the reaction orders, R_B, R_A and R_X, when

$$R_B = (dE^p/d\log v)^{-1} - 1 \qquad (2)$$

$$R_A = 1 - R_B + (R_B + 1)dE^p/d\log C_A - R_I \qquad (3)$$

$$R_X = (R_B + 1)dE^p/d\log C_X \qquad (4)$$

E^p is expressed in dimensionless form accomplished by division of the value measured in volts by $(\ln 10)RT/F$. The last term in eqn (3) refers to the reaction order in some species formed in the reaction that further participates, usually in an inhibiting way. The value of R_I is most often 0. These equations were verified by comparison with theoretical results for a number of mechanisms.

It was proposed that eqns. (2)–(4) could be used to derive the rate laws of complex and competing mechanisms directly from experimental data without resorting to theoretical calculations.[3] This would then seem to offer the possibility of assigning mechanisms to processes that are of such complexity that it is not feasible to carry out theoretical calculations without making severe assumptions. However, the approach has been sharply criticized by Savéant and co-workers.[5,6] They claim that the method

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* Part IV, see Ref. 4.

0302-4369/84 $2.50

fails when a reaction is controlled by more than a single rate determining step.[5,6] If Savéant's allegations are, in fact, true the "reaction order approach" to LSV is indeed limited.

It is the purpose of this paper to show that the criticisms[5,6] of the "reaction order approach" to LSV are not valid and to show explicitly how the method can be used for complex and competing reaction mechanisms of B. Furthermore, it is demonstrated that the approach is not only capable of providing the mechanism of an electrode process but also the rate constants providing that the rate law can be expressed as two limiting cases at the extremes of substrate concentration.

RESULTS AND DISCUSSION

The rate laws for most competing and complex reaction mechanisms reduce to two limiting cases at the extremes of the concentration of one of the reactants. There are other cases in which the rate constants are separable from the concentration terms in the rate law. The complexities of the reactions of the latter type are usually not detectable by kinetic techniques. Mechanisms of the former type are more amenable to kinetic studies and experiments can readily be designed to show that the rate of the reaction is controlled by more than a single step. This paper is addressed to the study of reactions of intermediate B of this type by LSV.

It has recently been shown that the electrode response to competing and complex mechanisms of reactions of B during analysis by direct kinetic techniques such as derivative cyclic voltammetry and double potential step chronoamperometry can be predicted from those of the two limiting cases.[7] The electrode response of the two limiting cases could be expressed in terms of linear equations in which C_A has different exponents. By expressing C_A in terms of multiples (n) of the value of C_A where the equations for the limiting cases intersect, the response in the intermediate concentration range could be defined by simple arithmetical procedures. Here, this same approach is adopted to the LSV response to competing and complex mechanisms.

The "reaction order approach" for the LSV response to a competing mechanism. Consider the competing first (5) and second (6) order reactions of B described by rate law (7). At some value of C_B the two terms within parentheses will be equal and the instantaneous

$$\mathrm{B} \xrightarrow{k_5} \mathrm{P}_5 \tag{5}$$

$$2\,\mathrm{B} \xrightarrow{k_6} \mathrm{P}_6 \tag{6}$$

$$\mathrm{Rate} = (k_5 + k_6 C_B) C_B \tag{7}$$

Scheme 1. Mechanism 1.

value of the reaction order in B, R_B will be equal to 1.5. Experimentally, we do not measure instantaneous reaction rates but rather measurements are made over finite time intervals. Under these conditions, the apparent value of R_B over that time interval will be 1.5 when the average value of C_B is such that $k_5 = k_6(C_B)_{\mathrm{average}}$. This value of the concentration, C_B°, during electrode generation of B will be associated with a particular substrate concentration, C_A°. These considerations can be used to developed the LSV response to mechanism (5)+(6).

The two limiting cases for this competing mechanism are when $k_5 \gg k_6 C_B$ and when $k_5 \ll k_6 C_B$, *i.e.* the EC and EC(dim) mechanisms, respectively. The LSV responses to these two mechanisms are given by eqns. (8)[8] and (9),[9] in which E^{rev} is the reversible

$$E^{\mathrm{p}} - E^{\mathrm{rev}} = -1.134 + \tfrac{1}{2} \log k_5/v \tag{8}$$

$$E^{\mathrm{p}} - E^{\mathrm{rev}} = -0.981 + \tfrac{1}{3} \log k_6 C_A/v \tag{9}$$

potential for reaction (1), E^{p} and E^{rev} are expressed in units of (ln 10) RT/F and v is in units of 1/s. At a given value of v, E^{p} is independent of C_A for reaction (5) and directly dependent on $\log C_A$ for reaction (6). Thus, plots of (8) and (9) will have slopes of 0 and ⅓, respectively, and intersect at $C_A = 0.348 k_5^{3/2}/k_6 v^{1/2}$. In the intermediate range of C_A, a plot of $E^{\mathrm{p}} - E^{\mathrm{rev}}$ will increase in slope from 0 to ⅓. The problem that remains is to define the curve in this region.

Since we are interested in relative E^{p} in the intermediate concentration region it is not necessary to include E^{rev} in the analysis. It is convenient for the slopes of the two limiting cases to differ by one unit which directly reflects that R_B changes by 1 in going from one limiting case to the other. This is the case when $(3\,E^{\mathrm{p}})_{\mathrm{rel}}$ is plotted *vs.* the appropriate function of C_A. The

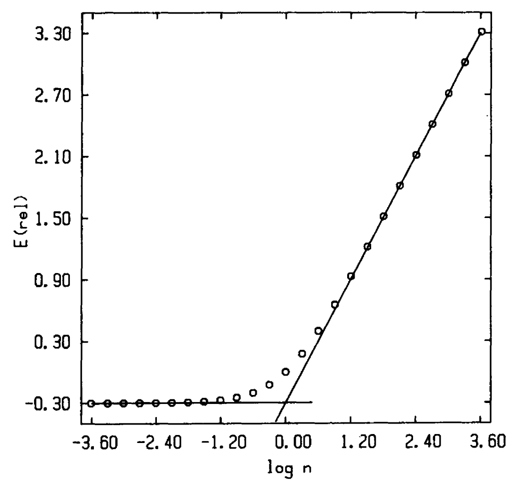

Fig. 1. A plot of 3 E^{p}(rel) *vs.* log n for mechanism 1.

subscript rel indicates that the values are relative. Our starting point is where the apparent value of R_{B} is 1.5. We can assign a value of 0 to $(3\,E^{\mathrm{p}})_{\mathrm{rel}}$ at this point on the curve and since C_{A}° is unknown and must be determined experimentally, the concentration scale can be expressed as multiples (n) of C_{A}°. The function of n which is to be equated to $(3E^{\mathrm{p}})_{\mathrm{rel}}$ can be formulated so that the co-ordinates of our starting point are (0,0) and is consistent with the known concentration dependence of the two limiting cases. The equality expressed in eqn. (10)

$$(3\,E^{\mathrm{p}})_{\mathrm{rel}}=\log{(n+1)/2} \qquad (10)$$

fulfills these requirements. At small values of n, $(3\,E^{\mathrm{p}})_{\mathrm{rel}}$ is independent of n(*i.e.* C_{A}) while the quantity depends directly on log n when the latter is large. Since R_{B} is expected to vary smoothly with n,[7] and this variation is directly related to E^{p},[3] eqn. (10) can be expected to be valid for all values of n. The curve calculated using eqn. (10) is illustrated in Fig. 1. The straight lines of 0 and unit slope are for the two limiting cases. It is readily confirmed that the intersection of the straight lines is at log n=0 by considering $n \ll 1$ and $n \gg 1$ which results in two equations, $(3\,E^{\mathrm{p}})_{\mathrm{rel}}=\log{1/2}$ and $(3\,E^{\mathrm{p}})_{\mathrm{rel}}=\log(n/2)$, respectively. Eliminating $(3\,E^{\mathrm{p}})_{\mathrm{rel}}$ from the two equations results in log n=0 at the intersection. The limitations regarding the errors involved in the procedure have been discussed.[7]

In order to use this "reaction order approach" to LSV mechanism analysis it is only necessary to carry out E^{p} measurements as a function of C_{A} and show that the curvature is that predicted by eqn. (10) for this competitive mechanism. A consistent data fit allows the rate law to be assigned. To this point we have not resorted to any theoretical calculations. The effect of C_{A} on E^{p} for the two limiting cases is evident from eqn. (3) where R_{A} and R_{I} are 0. Also, it is not necesary to know E^{rev} for charge transfer reaction (1) since we have only dealt with relative potentials.

Rate constants can be evaluated once the value of C_{A}° has been determined. This can be done using $(3\,E^{\mathrm{p}})_{\mathrm{rel}}$ values extrapolated to the limiting cases in eqns. (8) and (9). Both (8) and (9) require that it is possible to measure E^{rev} for charge transfer reaction (1). If this is not feasible, only the relative values can be evaluated from C_{A}° as discussed earlier.

A distinct advantage of LSV over other electrochemical techniques is that the reaction orders in A and B are readily separable. It is evident from eqn. (2) that R_{B} is known directly from $\mathrm{d}E^{\mathrm{p}}/\mathrm{dlog}v$. This offers an alternative method to determine C_{A}°. Thus, if $\mathrm{d}E^{\mathrm{p}}/\mathrm{dlog}\,v$ is determined as a function of C_{A}, C_{A}° will be that value of substrate concentration where R_{B}=1.5. In terms of n, we again have three distinct cases which must be satisfied by the function of n which can be equated to R_{B}. They are n=1(R_{B}=1.5), $n \ll 1$ (R_{B}=1) and $n \gg 1$ (R_{B}=2). Eqn. (11) satisfies these requirements and illustrates how R_{B} varies with n.

$$R_{\mathrm{B}}=1+n/(n+1) \qquad (11)$$

A plot of log R_{B} *vs.* log$(1+n/(n+1))$ is shown in Fig. 2. Between log n equal -0.301 and $+0.301$ the curve is linear. Thus, C_{A}° can be located from correlation of R_{B} with log C_{A} in the region where R_{B} ranges from about 1.3 to 1.7.

General procedure for constructing E^{p} vs. C_{A} *curves for competing and complex mechanisms.* After deriving the rate law for the mechanism the reaction orders for the limiting cases can be substituted into eqn. (3) to give the corresponding $\mathrm{d}E^{\mathrm{p}}/\mathrm{d}\log C_{\mathrm{A}}$. These will either be 0 or integral fractions. A common multiple (m) is chosen so that the slopes differ by one unit. If, for example, the two slopes are ⅓ and ½ multiplying

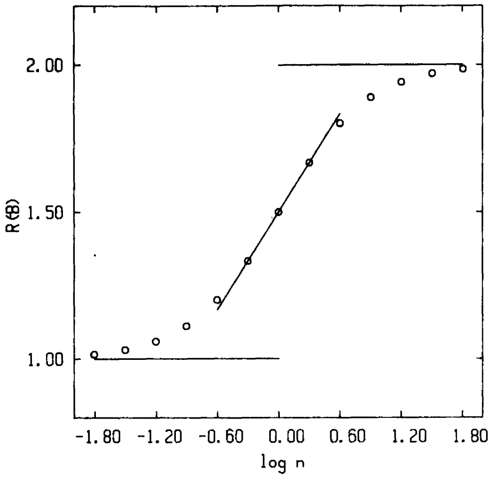

Fig. 2. A plot of reaction order R_B *vs* log *n* for mechanism 1.

by 6 gives slopes of 2 and 3. The next step is to find the function of *n*, f(*n*) which satisfies eqn. (12).

$$(m\,E^P)_{rel} = \log f(n) \qquad (12)$$

When $n=1$, f(*n*) must equal 1 and when $n \ll 1$ or $n \gg 1$ the exponent of *n* in f(*n*) must equal the corresponding slope after multiplication by *m*. Thus, f(*n*) will consist of *n* raised to some power either multiplied or divided by $(n+1)/2$ depending upon whether the slope increases or decreases with increasing *n*, respectively. For example, if the slope goes from 2 to 3 with increasing *n*, $f(n)=n^2(n+1)/2$, while $f(n)=2n^3/(n+1)$ if the change in slope is 3 to 2. Thus, the exponent of *n* in f(*n*) is the slope at the low concentration limit. The procedure is illustrated in the following paragraphs with several examples of competing and complex mechanisms.

Table 1. Quantities for constructing "reaction order approach" curves for competing and complex electrode mechanisms.

Mechanism[a]	$dE^P/d\log C_A$ $n \ll 1$	$n \gg 1$	m	f(n)
1	0	⅓	3	$(n+1)/2$
2	⅓	⅔	3	$n(n+1)/2$
3	⅓	0	3	$2n/(n+1)$
4	⅔	½	6	$2n^4/(n+1)$

[a] The mechanisms are defined in the text.

In Table 1, mechanism 1 refers to the competing first and second order reactions of B, eqns. (5) and (6), which has already been discussed. Using eqn. (3), the two limiting values of $dE^P/d\log C_A$ are 0 and ⅓ which requires that *m* equal 3. The corresponding f(*n*) is $(n+1)/2$, obtained as $n^0(n+1)/2$ from the procedure outlined.

Mechanism 2 is another example of a competing mechanism in which the reaction order in A changes from 0 at low C_A to 1 at the high concentration limit. This competing mechanism with

$$2\,B \xrightarrow{k_{13}} P_{13} \qquad (13)$$

$$B + A \underset{k_{-14}}{\overset{k_{14}}{\rightleftarrows}} C_{14} \qquad (14)$$

$$C_{14} + B \xrightarrow{k_{15}} P_{15} \qquad (15)$$

$$\text{rate} = (k_{13} + k_{15}K_{14}C_A)C_B^{\,2} \qquad (16)$$

Scheme 2. Mechanism 2.

rate law (16) could correspond to competing ion radical dimerization and ion radical–substrate coupling. The values of $dE^P/d\log C_A$ for the two limiting cases are ⅓ and ⅔ as indicated in Table 1. Thus, $m=3$ and $f(n)=n(n+1)/2$.

The most simple example of a complex mechanism in which the rate determining step changes with concentration is mechanism 3.

$$B \underset{k_{-17}}{\overset{k_{17}}{\rightleftarrows}} C_{17} \qquad (17)$$

$$C_{17} + B \xrightarrow{k_{18}} P_{18} \qquad (18)$$

$$\text{rate} = (k_{17}k_{18}/(k_{-17} + k_{18}C_B)C_B^{\,2} \qquad (19)$$

Scheme 3. Mechanism 3.

At the low concentration limit R_B is 2 and changes to 1 at the high concentration limit. The corresponding values of $dE^P/d\log C_A$ are ⅓ and 0 which again calls for $m=3$ and $f(n)=2n/(n+1)$.

The last entry in Table 1 refers to mechanism 4. In this case $R_A=1$ and R_B varies from 2 to 1 between the two limiting

$$B+A \underset{k_{-20}}{\overset{k_{20}}{\rightleftharpoons}} C_{20} \tag{20}$$

$$C_{20}+B \xrightarrow{k_{21}} P_{21} \tag{21}$$

$$\text{rate}=(k_{20}k_{21}/(k_{-20}+k_{21}C_B))C_B{}^2C_A \tag{22}$$

Scheme 4. Mechanism 4.

cases. Substituting the appropriate reaction orders in eqn. (3) results in $dE^P/d\log C_A$ of ⅔ ($n \ll 1$) and ½ ($n \gg 1$). Thus, $m=6$ and $f(n)=2n^4(n+1)$.

Justification of the numerical procedures used in the "reaction order approach" for electrode mechanism analysis. In an earlier paper[7] the electrode response data calculated by the "reaction order approach" was compared directly to theoretical data obtained by digital simulation and by other procedures. An excellent correspondence was found. That any possible differences must be small is readily shown by the following arguments. If a rate law can be viewed as two limiting cases and an intermediate one in which the characteristics of both of the limits are present and dependent upon concentration there will be a concentration at which the apparent rate law is half way between the extremes. The apparent rate at this point will differ by a factor of 2 from that predicted for either of the extremes operating alone. At any other concentration the apparent rate will approach that predicted by one or the other of the limiting cases. Therefore, the maximum difference between the observed rate and that for one or the other of the extremes is a factor of 2 and this will get smaller on either side of the midpoint. Thus, the procedure leaves a relatively small margin for error.

A test for consistency in the analysis. For Mechanism 1, eqn. (10) gives the relationship between E^P and the substrate concentration at a particular value of v. Equation (10) assumes $(3E^P)_{rel}$ equal to zero at n equal to 1 at this sweep rate. Since the point of intersection between the curves for the two limiting cases of this mechanism is proportional to $v^{-1/2}$, the effect of doubling v is to shift the point of intersection by $-½\log 2$ on the log n axis. Calculating E^P values using (10), along with $dE^P/d\log v$ for the limiting cases, and two different sweep rates provides the opportunity to test the consistency of the concentration dependence predicted by eqn. (10) with the sweep rate dependence predicted by eqn. (2) in conjunction with eqn. (11). This was done by varying the sweep rate by factors of 2 and 4. The peak potential differences (ΔE^P) are summarized in Table 2. The values without parentheses were obtained from eqn. (10) while those in parentheses were calculated assuming eqns. (2) and (11). The values obtained by the two different methods varied by no more than a few hundredths of a millivolt showing the consistency of eqn. (10) with (2) and (11) for this mechanism.

Table 2. The dependence of electrode peak potentials on substrate concentration and voltage sweep rate from Mechanism 1.[a]

log n	$\Delta E^P(v_2/v_1=2)$[b]	$\Delta E^P(v_2/v_1=4)$[b]
−3.612	8.91(8.91)	17.82(17.82)
−2.709	8.89(8.90)	17.78(17.79)
−2.408	8.90(8.89)	17.80(17.77)
−2.107	8.87(8.87)	17.74(17.73)
−1.806	8.85(8.84)	17.70(17.67)
−1.505	8.79(8.78)	17.57(17.54)
−1.204	8.66(8.66)	17.33(17.30)
−0.903	8.45(8.44)	16.91(16.87)
−0.602	8.13(8.10)	16.26(16.19)
−0.301	7.68(7.64)	15.36(15.26)
0	7.18(7.13)	14.35(14.24)
0.301	6.83(6.68)	13.35(13.35)
0.602	6.47(6.36)	12.70(12.72)
0.903	6.23(6.17)	12.28(12.33)
1.204	6.09(6.06)	12.05(12.11)
1.505	6.00(6.00)	11.90(11.99)
1.806	5.98(5.97)	11.85(11.93)
2.107	5.97(5.96)	11.83(11.90)
2.408	5.96(5.95)	11.82(11.89)
2.704	5.96(5.94)	11.80(11.88)

[a] At 298.1 K. [b] The potentials are expressed in millivolts. The values without parentheses were calculated using eqn. (10) while those in parentheses were obtained using eqns. (2) and (11).

Similar analysis of the predicted response for Mechanism 2 is instructive. In this case the sweep rate dependences for the two limiting cases are identical. This requires that the point of intersection between the two limiting curves be independent of v and thus ΔE^P is exactly that predicted by eqns (2) and (11) regardless of what function is chosen for the concentration dependence. While this may seem to be a trivial result it does support the validity of the method. That is, $\Delta E^P/\Delta\log v$

remains constant while the reaction passes through the transition region between the two mechanisms.

The results of the analyses for consistency on the complex Mechanism 3 and Mechanism 4 were likewise satisfactory. Only small differences were observed between the $\Delta E^p/\Delta \log v$ values predicted by the two methods.

Although there may be mechanisms for which the "Reaction Order Approach" does not give as close correspondence to other methods for predicting the LSV response as those that have been examined here, it appears safe to conclude that any differences that may be observed will be small and not give rise to errors larger than those expected in experimental investigations.

CONCLUSIONS

The "reaction order approach" allows one to predict the LSV response for competing and complex mechanisms from that for limiting cases at the extremes of the substrate concentration. The LSV response for simple mechanisms of which type the limiting cases belong, can be predicted directly from the rate law and eqns. (2) to (4).

The main point of the original formulation of this approach[3] was that the rate law for an electrode reaction of unknown mechanism can be derived from eqns. (2) to (4) directly from experimental data without making any assumptions or approximations. These equations were verified by comparison with results derived by the integration of the differential equations describing the processes. These comparisons were with theoretical results from simple mechanisms and this was simply because those were the only ones available. But the main power of this approach was clearly stated to be in the analysis of processes for which theoretical data are either not available or cannot be obtained without invoking serious assumptions and approximations. The results presented in this paper establish without doubt that the original formulation and suggestions regarding competing and complex mechanism were indeed correct.

REFERENCES

1. Parker, V. D. *Acta Chem. Scand. B 34* (1980) 359.
2. Ahlberg, E. and Parker, V. D. *Acta Chem. Scand. B 35* (1981) 117.
3. Parker, V. D. *Acta Chem. Scand. B 35* (1981) 259.
4. Parker, V. D. *Acta Chem. Scand. B 35* (1981) 373.
5. Amatore, C., Pinson, J. and Savéant, J. M. *J. Electroanal. Chem. 137* (1982) 143.
6. Amatore, C. and Savéant, J. M. *J. Electroanal. Chem. 144* (1983) 59.
7. Parker, V. D. *Acta Chem. Scand. B 38* (1984) 165.
8. Nicholson, R. S. and Shain, I. *Anal. Chem. 36* (1964) 706.
9. Nicholson, R. S. *Anal. Chem. 37* (1965) 667.

Received May 11, 1983.