

Qualitative Mechanism Analysis by Linear Sweep Voltammetry

VERNON D. PARKER

Laboratory for Organic Chemistry, Norwegian Institute of Technology, University of Trondheim, N-7034 Trondheim-NTH, Norway

Rules are suggested for predicting electrode potential responses to changes in sweep rate, substrate concentration and additional reactant concentration during linear sweep voltammetry. Use of the rules makes mechanistic analysis possible in cases where the theoretical response has not been determined. The analysis is illustrated with reference to the reaction between 9,10-diphenylanthracene cation radical and pyridine in acetonitrile. The simple rules invariably give the theoretical sweep rate response without resort to calculations. For very complex reaction schemes it may not be possible to predict the substrate concentration response without more detailed analysis.

Electrode reactions of organic molecules most often involve complex mechanisms with chemical reactions of intermediates interposed between heterogeneous and homogeneous electron transfer steps. In spite of the complexity, kinetic techniques have developed which allow the unravelling of some of these mechanisms. Linear sweep voltammetry (LSV) has emerged as one of the most powerful tools for the qualitative, and sometimes quantitative, mechanism analysis. The latter is primarily due to the early work of Nicholson and Shain¹ and the extensive calculations of Savéant and coworkers.^{2–7}

When the initial charge transfer is rapid compared to the rate of ensuing chemical reactions and to the voltage sweep rate (ν), the current-voltage curve has the characteristics of a purely kinetic wave. This is most often the case for the oxidation or reduction of aromatic compounds at low sweep rates and it is under these conditions that LSV can be used for mechanism analysis. The electrode peak potential (E^p) is influenced by three variables; ν , the substrate concentration (C^o) and the concentration of additional reactants (C^x). Thus, $dE^p/d \log \nu$,

$dE^p/d \log C^o$, and $dE^p/d \log C^x$, provide a highly effective mechanistic diagnosis once the diffusion-kinetic problem for the particular mechanism has been solved.^{1–7} This normally involves the development and the solution of integral equations based upon initial and boundary conditions. While the latter is not such a formidable task for those who are versed in the calculational techniques, it is most often beyond the scope of an organic chemist's involvement in the electrode problem. Therefore, potential mechanistic analyses may be set aside because the mechanistic possibilities have not previously been analyzed. It is the purpose of this note to develop general rules for predicting the LSV response to the variables mentioned earlier without resort to any calculations.

For most electrode mechanisms, the three electrode potential slopes are integral fractions, 2/3, 1/2, 1/3 or 1/4, of $(\ln 10)RT/F$ (equal to 59.1 mV at 25 °C) where R is the gas constant, T the absolute temperature, and F is the Faraday constant. Thus, slopes of 39.4, 29.6, 19.7 or 14.8 mV/decade are predicted. The expected values depend on what particular steps, in relation to the rate determining step (RDS), are involved in the mechanism. In order to illustrate the rules, the following symbolism for mechanism designation, patterned after that used by Savéant and coworkers^{2–7} will be used to describe the electrode processes:

- e = charge transfer at the electrode
- e_h = homogeneous electron transfer regenerating substrate
- e/e = electron transfer before dimerization
- c = homogeneous chemical reaction, first or pseudo first order with unspecified reactant
- c^x = homogeneous chemical reaction, pseudo first order with reactant x

c/c = second order dimerization of the intermediate
 c/c^s = reaction between intermediate and substrate

Any of the symbols written as a capital letter indicates the RDS. The most outstanding difference between this symbolism and that previously used²⁻⁷ is the designation of solution electron transfers as e_h . Savéant and coworkers refer to this as d , for disproportionation, and this can lead to confusion since disproportionation implies reactions between two like species to give two different species.

The rules, which assume an initial charge transfer (e), $A \pm e \rightleftharpoons B$, for predicting the numerical values of the various slopes can be summarized as in Table 1.

Table 1. The rules.

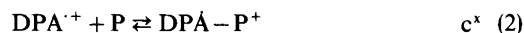
	Electron transfer steps before or during RDS	mV/decade
1. $dE/d \log v$	e	29.6
	e, e_h	19.7
	e, E_h	19.7
	e/e	19.7
	e, e	14.8
2. $dE/d \log C^x$	If c^x appears before the RDS or C^x is the RDS, the slope will be the same as $dE/d \log v$. Otherwise, this term is equal to zero.	
3. $dE/d \log C^o$	$k_{app} C_B$	0
	$k_{app} C_B^2$	19.7
	$k_{app} C_B^2 / C_A$	0
	$k_{app} C_A C_B$	29.6
	$k_{app} C_A C_B^2$	39.4

In rule 3, k_{app} refers to the apparent rate constant for the mechanism derived for the reaction of intermediate B, using the steady state approximation if necessary. The concentration terms, C_A and C_B , refer to the substrate and intermediate, respectively. Terms involving the concentration of X only affect this slope in exceptional cases and are not included in the rate equations of rule 3. In using the rules, the first step is to write down all of the steps in the mechanism and to assign the appropriate symbol to each step. The rate law can then be derived and the slopes predicted from the rules.

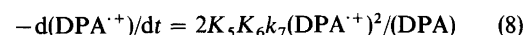
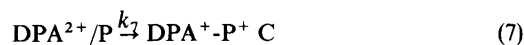
Rule 1 is applicable to all known cases as is rule 2 with the exception of some complex ee systems. The only known cases where rule 3 does not apply

involve reversible protonation equilibria before the RDS and an additional concentration term, that of the conjugate base of the proton donor appears in the denominator of the rate equation.

In order to illustrate the application of the rules we can look at a specific example which has recently been treated.⁸ The mechanism of the reaction between 9,10-diphenylanthracene (DPA) cation radical and pyridine (P) was recently suggested to take place according to eqns. (1) to (3) where k_3 is the RDS.⁹ The mechanism can be designated as $e-c^x-E_h$, and assuming that step (2) is in equilibrium, the rate law is $-d(DPA^+)/dt = k_{app}(DPA^+)^2(P)$.



The rules stated predict the slopes to be 19.7, 19.7 and 19.7 mV/decade. This mechanism has in fact been analyzed previously.⁶ An alternative mechanism, which features an initial π -complex equilibrium (5) is illustrated below for the case where k_7 is rate determining. This mechanism has previously been shown to hold for a number of cation radical - nucleophile reactions.¹⁰



Assuming that (5) and (6) are in equilibrium leads to rate law (8). The mechanism can be designated as $e-c^x-e_h-C$ and the v and C^x responses are predicted to be 19.7 mV/decade while the response is predicted to be independent of C^o . The experimental determination of the slopes showed that at low DPA concentration the values are precisely those predicted by the complexation mechanism.⁸

The resolution of the DPA^+ -pyridine mechanism by LSV is noteworthy in that up until this year, the mechanism was believed to be firmly established

as being of the $e-C^x-e_n$ type since homogeneous kinetic studies^{11,12} had indicated that the reaction is first order both in DPA^+ and P. Analysis of the reaction by a variation of LSV was recently made and the slope found was not the expected 29.6 mV which led the author to erroneously¹³ question the validity of using theoretical equations without an experimental calibration. This should serve as a reminder that mechanisms are correct only as long as they account for all the experimental facts.

The simple rules stated here can be used as a convenient guide in the investigation of the mechanisms of electrode reactions by LVS. The ν dependence should be predicted by rule 1 for all cases where charge transfer at the electrode is the initial step in the mechanism. Rules 2 and 3 will be valid for practically all cases and exceptions have been noted in the previous paragraphs. There will no doubt arise complicated mechanisms for which detailed analysis cannot be avoided. However, the observation that the rules given above do not apply to a particular case is a significant mechanistic aid in itself since all of the common possibilities are then ruled out.

In conclusion, it must be emphasized that the rules stated are generalizations based upon the detailed calculations that have been carried out¹⁻⁷ and are given as an aid to mechanism analysis when the theoretical responses have not been determined. This should not be interpreted to mean that detailed analysis should not be carried out when facilities are available. Quite on the contrary, it is the author's opinion that mechanism analysis should be verified by more than one independent technique.

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Received November 12, 1979.