

Electrode Mechanism Analysis by Linear Sweep Voltammetry.

II. Application of Derivative Cyclic Voltammetry

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A linear logarithmic relationship between the derivative peak ratio (R'_i) and the inverse of the voltage sweep rate ($1/v$) is described for several electrode mechanisms. The slopes, $d(\ln R'_i)/d(\ln v^{-1})$, are characteristic of the mechanisms of the processes, and mechanism analysis can be carried out without resort to fitting experimental data to theoretical working curves. Results of theoretical calculations are presented for four different mechanism types including; ECE_h , Disproportionation, $EC(dim)$ and Radical-Substrate Dimerization. The $d(\ln R'_i)/d(\ln v^{-1})$ analysis clearly distinguishes between the two first order mechanisms while the dimer forming mechanisms require an additional relationship. The latter are distinguished by another linear relationship which holds for some of the mechanisms, $d(\ln \Delta E^p)/d(\ln v^{-1})$, where ΔE^p refers to the peak potential difference between the forward and backward scans during DCV. The analysis is demonstrated by studies on the protonation of anthracene anion radical, an ECE_h mechanism which has been well established by other techniques.

Linear sweep voltammetry is a powerful tool for electrode mechanism analysis. Rules for predicting the electrode response have recently been presented.¹ When used in conjunction with normalized potential sweep voltammetry (NPSV), a technique recently described² which gives a direct comparison of theoretical and experimental data, mechanisms for purely kinetic waves can be assigned with a high degree of certainty. The method is not applicable to processes which do not exhibit

purely kinetic waves and the rate of the kinetic step and mechanism analysis in these cases must be made using other electroanalytical techniques. The mechanism of the reaction is then assigned on the basis of the best fit to theoretical working curves calculated for the various mechanistic possibilities. The latter is often a very uncertain procedure because the working curves for different mechanisms are very similar.

During the development of derivative cyclic voltammetry (DCV) as a highly precise kinetic method,³ it was found that equation (1), where R'_i refers to the derivative peak ratio and

$$\ln R'_i = m \ln(k/a) + c \quad (1)$$

a is nFv/RT , described the response for the ECE_h mechanism.* In (1) m and c are the correlation parameters for data in the R'_i range equal to 0.25 to 0.7. We have now carried out calculations for other mechanisms and find that (1) is applicable with the values of m and c being dependent upon the particular mechanism. The only mechanism that we have found not to give data in accord with (1) is the simple EC case. Here, we present the results of the calculations pertaining to (1) as well as another linear relationship which holds in some cases. The method is developed on an established mechanism, the protonation of anthracene anion radical by phenol in N,N -dimethylformamide (DMF).

* This mechanism is commonly designated by the somewhat non-descriptive term, $ECE(\text{nuance})$.⁴ We use the term, ECE_h where the h indicates that the second electron transfer takes place in solution as defined in Ref. 1.

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Table 1. Description of the mechanisms and simulations for DCV mechanism analysis.

Mechanism	Reaction scheme	Rate equation	Digital simulation
ECE _n	A ± e ⁻ ⇌ B B \xrightarrow{k} C B + C ⇌ A + D	kC _B	(C _A) _{t+1} = (C _A) _t + rate (C _B) _{t+1} = (C _B) _t - 2(rate)
Disproportionation	A ± e ⁻ ⇌ B 2 B $\xrightleftharpoons{K_{eq}}$ A + C C \xrightarrow{k} D	kK _{eq} C _B ² /C _A	(C _A) _{t+1} = (C _A) _t (C _B) _{t+1} = (C _B) _t - 2(rate)
EC(dim)	A ± e ⁻ ⇌ B 2 B \xrightarrow{k} C	kC _B ²	(C _A) _{t+1} = (C _A) _t (C _B) _{t+1} = (C _B) _t - 2(rate)
Radical-Substrate (case 1)	A ± e ⁻ ⇌ B A + B \xrightarrow{k} C B + C ⇌ A + D	kC _A C _B	(C _A) _{t+1} = (C _A) _t (C _B) _{t+1} = (C _B) _t - 2(rate)
Radical-Substrate (case 2)	A ± e ⁻ ⇌ B A + B $\xrightleftharpoons{K_{eq}}$ C B + C \xrightarrow{k} A + D	kK _{eq} C _B ² C _A	(C _A) _{t+1} = (C _A) _t (C _B) _{t+1} = (C _B) _t - 2(rate)

Table 2. Correlation parameters of derivative cyclic voltammetric data for various electrode mechanisms.

Mechanism	Switching potential ^a	m ^b	c ^c	r ^d
ECE _n	200	-0.318	-1.226	0.9996
	300	-0.351	-1.466	0.9993
	400	-0.363	-1.622	0.9999
	500	-0.378	-1.754	0.9999
EC(dim)	200	-0.295	-1.162	0.9998
	300	-0.307	-1.351	0.9999
	400	-0.311	-1.475	0.9996
	500	-0.318	-1.484	1.0000
Disproportionation	200	-0.229	-1.363	1.0000
	300	-0.237	-1.600	0.9996
	400	-0.247	-1.783	0.9990
	500	-0.263	-1.963	0.9994
Radical-Substrate (case 1)	200	-0.363	-1.230	0.9997
	300	-0.373	-1.398	0.9996
	400	-0.378	-1.507	0.9996
	500	-0.383	-1.593	0.9997
Radical-Substrate (case 2)	300	-0.319	-0.952	0.9998

^a Difference between the switching potential and the reversible potential. ^b Slope. ^c Intercept. ^d Correlation coefficient for analysis of theoretical data for the R_i range from 0.25 to 0.70 according to Ref. 3.

RESULTS AND DISCUSSION

Equation (1) can be transformed into a form relating only the experimental variables, R'_1 and v (the voltage sweep rate) to give (2) and noting that v is the only variable on the right-hand side, to equation (3). The slope m is then a parameter that can be determined

$$\ln R'_1 = m \ln(1/v) + m \ln(RT/kF) + c \quad (2)$$

$$\ln R'_1 = m \ln(1/v) + c' \quad (3)$$

without making any assumptions regarding the mechanism of the electrode process. Thus, if m varies according to the mechanism of the reaction following charge transfer, it can be used in mechanism analysis.

In order to determine how m varies with mechanism, calculations were carried out on a number of different mechanistic types. It should be pointed out, as was emphasized earlier,¹ that the electrode response depends upon the rate law describing the overall reaction. Thus, if two mechanisms predict the same rate law, the response for the two will be indistinguishable. The four reaction types; ECE_h, Disproportionation, EC(dim), and Radical-Substrate Coupling (2 cases) are summarized in Table 1 along with the digital simulation⁵ parameters for the kinetic schemes. In all cases v_{sim} was 1 mv/step and D_{sim} was 0.45 while k/a varied from zero to one. The number of volume elements (I_{max}) necessary at each time step t was determined from (4).⁶

$$I_{\text{max}} = 6(tD)^{1/2}, t = 1, 2, 3, \dots \quad (4)$$

In the calculations of the disproportionation mechanism, the substrate concentration was assumed to be unaltered by the kinetics. This approximation does not hold for very rapid

reactions with large values of kK_{eq} and a very thin reaction layer but is valid for the relatively slow reactions which can be studied by DCV. Also, the substrate concentration in the radical-substrate coupling mechanisms was assumed to be unaltered by the kinetics since substrate is consumed in one step but is regenerated in a succeeding one.

The theoretical results pertaining to equation (3) are summarized in Table 2. The value of $d(\ln R'_1)/d(\ln v^{-1})$ depends upon the difference between the switching and reversible potentials, $E_{\text{sw}} - E_{\text{rev}}$, and calculations were carried out for 200, 300, 400 and 500 mV. For ease of comparison, the data for $E_{\text{sw}} - E_{\text{rev}}$ equal to 300 mV for all of the mechanisms are summarized in Table 3. In Table 3 the symbols designating the reaction mechanisms are those previously used.¹ Those symbols with capital letters indicate the rate determining step and e_h designates a homogeneous electron transfer in contrast to the symbol for the electrode reaction, e .

In terms of mechanism analysis, we can divide the reactions into two groups according to whether or not dimeric products are formed. The ECE_h and Disproportionation mechanisms can give rise to the same non-dimeric products. The values of $d(\ln R'_1)/d(\ln v^{-1})$, -0.351 and -0.237 ($E_{\text{sw}} - E_{\text{rev}} = 300$ mV) differ significantly and thus the mechanisms are readily distinguished by the analysis. Of the three mechanisms resulting in dimeric products, the EC(dim) and Radical-Substrate (with rate determining electron transfer, case 2) mechanisms have slopes too close in magnitude to be distinguishable but both of these mechanisms have slopes distinct from the third, Radical-Substrate Coupling (case 1). The LSV slopes are included for comparison.

The data in Table 4 illustrate still another linear relationship for DCV mechanism analysis. In this case the slope determined is $d(\ln \Delta E^p)/d(\ln v^{-1})$ which results from equation (6) derived from

Table 3. A comparison of DCV and LSV mechanism analysis slopes.

Mechanism	Symbol	$d \ln R'_1 / d \ln(1/v)^a$	$dE^p / d \log v^b$	$dE^p / d \log C^{\circ b}$
ECE _h	$eC^x e_h$	-0.351	29.6	0
Disproportionation	$ee_h C^x$	-0.237	19.7	0
EC(dim)	$e/eC/C$	-0.307	19.7	19.7
Radical-Substrate	eC/C^s	-0.372	29.6	29.6
Radical-Substrate	$ec/c^s E_h$	-0.319	19.7	39.4

^a Correlation according to eqn. (2), $E_{\text{sw}} - E_{\text{rev}} = 300$ mV, $T = 298$ K. ^b At 298 K in mV/decade.

Table 4. The derivative peak separation in DCV mechanism analysis.^a

Mechanism	Symbol	$d(\ln \Delta E^P)/(\ln v^{-1})^b$
Disproportionation	$ee_n C^x$	0.107
EC(dim)	$e/eC/C$	0.076
Radical-Substrate-1 ^c	eC/C^s	negative
Radical-Substrate-2 ^d	$ec/c^s E_n$	~ 0

^a Correlations according to eqn. (6). ^b The slopes are nearly independent of $E_{sw} - E_{rev}$ with a standard deviation of about 3% in values from different $E_{sw} - E_{rev}$. ^c Case 1 in Table 1. The response in this case is unique in that as k/a increases, ΔE^P first decreases to values as low as about 51 mV as R'_i goes from about 1 to 0.3–0.4, and then increases at lower values of R'_i . ^d Case 2 in Table 2.

relationship (5). The linear equation (6) was found to hold

$$\ln \Delta E^P = m_\Delta \ln(k/a) + c \quad (5)$$

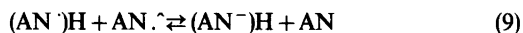
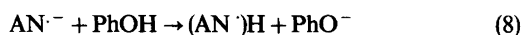
$$\ln \Delta E^P = m_\Delta \ln(v^{-1}) + c' \quad (6)$$

in the R'_i range, 0.20 to 0.45 for the EC(dim) and Disproportionation mechanisms and approximately for the Radical-Substrate mechanisms. Thus, DCV mechanism analysis is capable of distinguishing between all of the mechanisms summarized in Table 1.

Some further comments are in order regarding the dependence of ΔE^P on v^{-1} . The analysis cannot be applied to the ECE_n case because the peak on the backward scan of the current voltage curve becomes indistinct at large k/a and the derivative does not pass through zero. This in itself is very distinctive in

a qualitative way but makes a numerical determination of the slope impossible. The correlations for both case 1 and case 2 of the Radical-Substrate Coupling mechanism are also very distinctive. The peak separation ΔE^P for case 2 is nearly independent of v while it actually decreases to a value considerably lower than ΔE^P_{rev} for case 1 before beginning to increase again. This behaviour is very distinctive and is readily recognized. Thus, these mechanisms are very easily identified by the DCV analysis.

The protonation of anthracene anion radical by phenol in DMF has been studied by DCV,³ LSV,³ double potential step chronoamperometry^{3,7} and by cyclic voltammetry.⁷ The kinetic studies resulted in general agreement on the ECE_n mechanism. Thus, the reaction can be described by equations (7)–(10) where AN indicates anthracene. Since this is one of the few electrode processes for which sufficient data are available for mechanism assignment, the system can be used as a model to test techniques for consistency between experimental and theoretical data.



The data in Table 5 serve to verify the applicability of equation (3) to this system. The value of $d(\ln R'_i)/d(\ln v^{-1})$ was found to be equal to -0.379 ± 0.013 when $E_{sw} - E_{rev}$ was equal to 500 mV. The theoretical value (Table 2) is -0.378 . The very close

Table 5. Derivative cyclic voltammetric mechanism analysis of the protonation of anthracene anion radical by phenol.^a

[An]/mM	[PhOH]/mM	$v/V \text{ s}^{-1}$	$E_{sw} - E_{rev}/\text{mV}$	m^b
1.00	12.8	10, 20, 50	500	-0.374
1.00	102.3	50, 100, 200, 300, 400	500	-0.404
1.00	26.1	10, 30, 50, 100	500	-0.374
2.50	57.5	30, 50, 100, 200, 300	500	-0.369
1.50	51.6	30, 50, 100, 200, 300	500	-0.366
1.00	47.3	10, 30, 50, 100, 200	500	-0.375
0.50	57.5	30, 50, 100, 200, 300	500	-0.389

^a Measurements at 20 °C as described in Ref. 3, the solvent was DMF and the supporting electrolyte was Bu_4NBF_4 (0.1 M). ^b Slope according to eqn. (3), all correlation coefficients were 0.999.

agreement between experiment and theory indicates that the DCV slope is indeed a parameter which can be used in mechanism analysis. The other first order mechanism, Disproportionation,* predicts a slope of -0.263 under the measurement conditions and this is clearly out of the range of experimental error from the observed value. The standard deviation found in the measurements, ± 0.013 , corresponds to a 3.4% error level. Use of even the most precise measurement techniques for potential measurements during LSV mechanism analysis has recently resulted in $dE^p/d(\log v)$ values of about 19 ± 1 mV for second order reactions,^{8,9} which corresponds to approximately 5% error level. Thus, it appears that the DCV mechanism analysis has about the same capability for sensitivity as that for LSV.

In conclusion, we emphasize that the DCV mechanism analysis presented here compliments the corresponding LSV analysis. The two analyses are applicable in different situations. For very fast reactions following charge transfer, LSV can provide mechanism data even though the rate constants of the reactions of interest cannot be determined. The DCV analysis applies to slower reactions where the electrode generated intermediate can be observed by CV. Since equation (3) relates experimental parameters to obtain the DCV slope, the mechanism analysis can be made before assigning rate constants.

Finally, it would be desirable to test the DCV mechanism analysis on established mechanisms of all types. If one considers carrying out such a program it is quickly found that model systems just are not available. This has been emphasized^{1,10,11} by the recent studies on the pyridination of 9,10-diphenylanthracene cation radical, a reaction long believed to go by the ECE_n mechanism.¹² The more recent work shows that the reaction is much more complex than previously believed.

EXPERIMENTAL

Theoretical cyclic voltammograms were differentiated by the least squares procedure of Savitzky and Golay.¹³ The instrumentation, cells, electrodes, solvent purification and data handling

procedures were those reported in recent publications from this laboratory.^{3,10,14}

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* This mechanism is often regarded as a second order mechanism since the order in ion radical is 2. However, under the DCV conditions the apparent rate constant has the units of s^{-1} .