

Theory and Application of 2 Cycle Cyclic Voltammetry for the Study of the Kinetics of the Reactions of Electrode-generated Intermediates

Vernon D. Parker

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

Parker, Vernon D., 1986. Theory and Application of 2 Cycle Cyclic Voltammetry for the Study of the Kinetics of the Reactions of Electrode-Generated Intermediates. – *Acta Chem. Scand. B* 40: 50–54.

A double cyclic voltammogram is readily generated using a 2 cycle burst waveform. The ratio of the peak currents on the two cycles, $R_1 = I_2/I_1$, gives a direct measure of the concentration change of the substrate in the reaction layer resulting from the reaction of an electrode-generated intermediate. The base-line problem associated with ordinary cyclic voltammetry is essentially eliminated with this technique and problems arising from charge transfer kinetics are minimized. Theoretical data for two different electrode mechanisms are presented and shown to fit 5th order polynomial expressions. The method is demonstrated by kinetic studies of two different anion radical reactions. Measurement precision was observed to be of the order of $\pm 22\%$ of observed rate constants.

Although cyclic voltammetry (CV) using multiple triangular waveform cycles is often used in qualitative studies,¹ kinetic measurements invariably employ data from the first cyclic electrode potential perturbation. Recent work² has demonstrated that ordinary CV can provide quantitative kinetic data for clean electrode processes, *i.e.* Those that involve only Faradaic and electrical double layer charging currents. The latter condition is not always fulfilled for the reactions of organic ion radicals in aprotic solvents where other complicating processes are often involved. A viable alternative to ordinary CV is described here. The technique involves an electrode potential program consisting of two cycle bursts from the rest potential. Measurements are then made on the peak currents for the two cycles. Advantages of the method include (i) the baseline for the forward peak on both cycles is determined and used in evaluation of the peak currents and (ii) any complications due to heterogeneous charge transfer kinetics are greatly diminished since measurements are made on the same peak on both cycles.

Results and discussion

Qualitative Description of the Method. The waveform for 2 cycle CV consists of two cycle bursts from the rest potential where no Faradaic processes take place with adequate time between the bursts so that the electrode interface resumes the initial conditions. In this work a Hewlett Packard 3314A-1 Function Generator in the N Cycle Burst Mode was used to generate the appropriate electrode potential program. In all the work described here, an 800 mV ramp was used with $E_{sw} - E_{rev}$, the difference in switching and reversible potentials, equal to 300 mV.

In order to qualitatively demonstrate the range of response to be expected during 2 cycle CV, the reduction of fluoren-9-one (1.0 mM) in MeCN and in MeCN containing acetic acid (22 mM) was carried out. In the absence of HOAc, the process corresponds very closely² to Nernstian charge transfer. The 2 cycle CV at 100 V/s for this case is illustrated in Fig. 1a. The corresponding a cycle DCV (derivative CV) is shown in Fig. 1b. In the

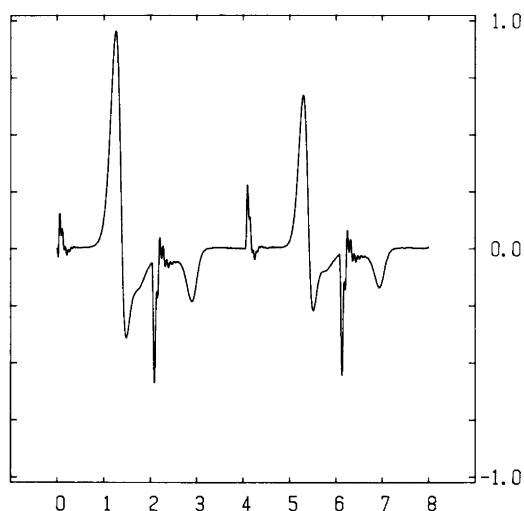
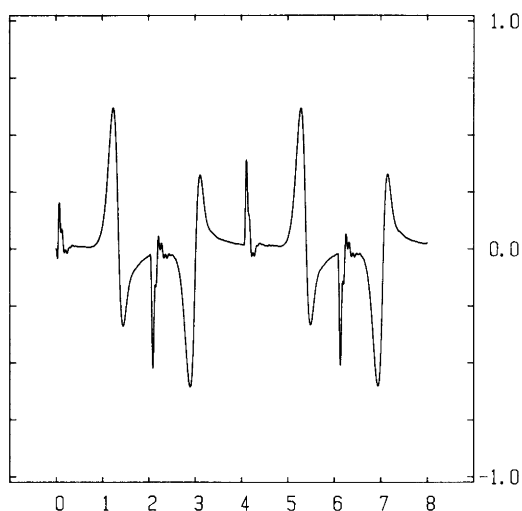
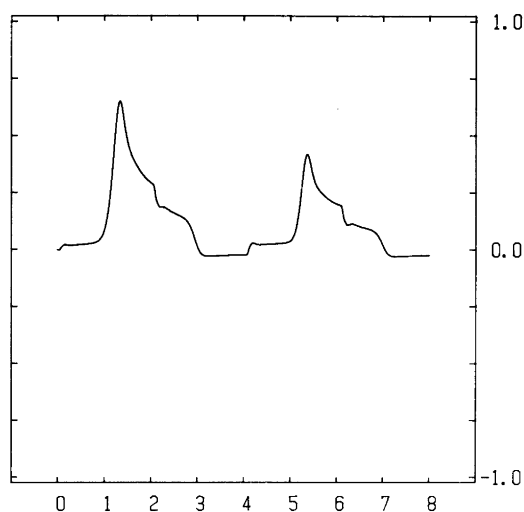
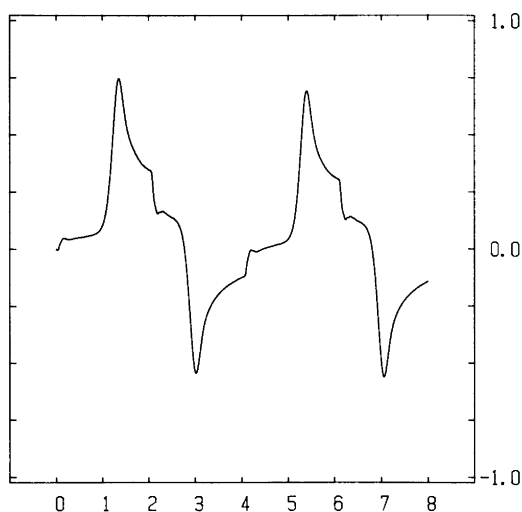


Fig. 1. 2 cycle CV (a) and 2 cycle DCV (b) for the reduction of fluoren-9-one (1.0 mM) in acetonitrile Bu_4NBF_4 (0.1 M) at 100 V/s. Start potential -1.10 V. vs. Ag/Ag^+ . Potential scale: 400 mV/division.

Fig. 2. 2 cycle CV (a) and 2 cycle DCV (b) for the reduction of fluoren-9-one (1.0 mM) in acetonitrile- Bu_4NBF_4 (0.1 M) containing HOAc (22 mM) at 100 V/s. Start Potential -0.90 V. vs. Ag/Ag^+ , 400 mV/division.

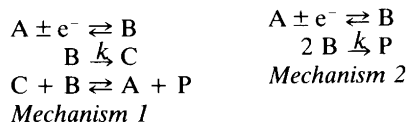
presence of acetic acid under the same conditions, no current for the oxidation of the corresponding anion radical could be detected (Fig. 2a) and the peak height on the second cycle is reduced to about 60% of that on the first cycle. The latter is due to the essentially complete pro-

tonation of the anion radical by acetic acid. The 2 cycle DCV for this process is shown in Fig. 2b.

Theoretical Data. Although a number of different data manipulation strategies are possible using the 4 peak currents obtained in 2 cycle CV, this

discussion of the method will be restricted to the relationship of R_1 , defined as the ratio of the peak current on the forward segment of the second cycle to that on the first, to the kinetics of the electrode generated intermediate.

Calculations were carried out on two common electrode reactions, the eCe_n (Mechanism 1) and the $eC(dim)$ (Mechanism 2) mechanisms. The theoretical data for these two mechanisms are tabulated in the first two columns of Tables 1 and 2.



The data were obtained by digital simulation³ using the integrated rate expressions^{4,5} in the calculation of the changes due to the kinetics.

The fit of the data for Mechanism 1 to a 5th order polynomial expression is shown in Fig. 3. The third columns in Tables 1 and 2 give the values of the kinetic parameters calculated from the poly-

Table 1. Theoretical 2 cycle cyclic voltammetry data for mechanism 1 (eCe_n).

$-\log k/a^a$	R_1^b	$-(\log k/a)_{calc}^c$	% error ^d
0.192	0.644		
0.347	0.657	0.342	1.2
0.493	0.671	0.393	0
0.648	0.688	0.653	1.2
0.794	0.706	0.799	1.2
0.949	0.727	0.948	0.2
1.095	0.750	1.093	0.5
1.250	0.776	1.246	0.9
1.396	0.803	1.397	0.2
1.551	0.831	1.554	0.7
1.698	0.856	1.700	0.5
1.852	0.879	1.855	0.7
1.998	0.898	1.992	1.4
2.153	0.914	2.153	0
± 0.7			

^a $a = Fv/RT$ where v is the voltage sweep rate.

^bDefined in the text.

^cCalculated from the polynomial expression described in Table 3.

^dThe error in data obtained in c.

Table 2. Theoretical 2 cycle cyclic voltammetry data for mechanism 2 ($eC(dim)$).

$-\log kC/a$	R_1^b	$-(\log kC/a)_{calc}^b$	% error ^b
0.192	0.624		
0.347	0.637	0.345	0.5
0.493	0.651	0.492	0.2
0.648	0.669	0.651	0.7
0.794	0.688	0.794	0
0.949	0.712	0.951	0.5
1.095	0.736	1.092	0.7
1.250	0.765	1.251	0.2
1.396	0.792	1.395	0.2
1.551	0.821	1.551	0
1.698	0.847	1.698	0
1.852	0.872	1.855	0.7
1.998	0.891	1.994	0.9
2.153	0.908	2.151	0.5
± 0.4			

^a C is the bulk concentration of the substrate.

^bAs in Table 1.

nomial expressions which are summarized in Table 3. Deviations between the real kinetic parameters and those derived from the polynomials

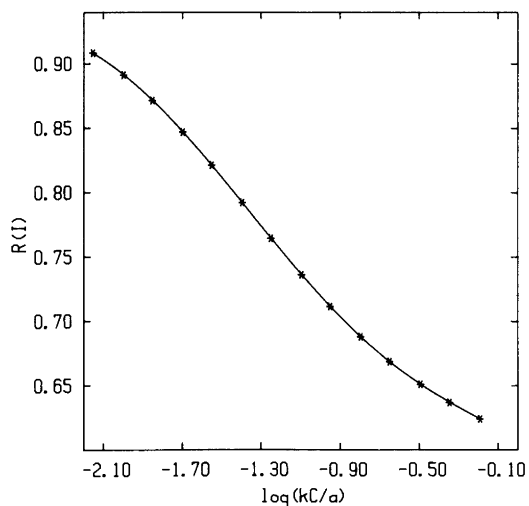
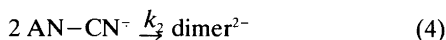
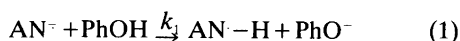


Fig. 3. Theoretical data for the eCe_n mechanism (*). The solid line is for the best fit with a 5th order polynomial expression.

are small for both sets of data and indicate that significant error will not be introduced from this source. The data in Table 3 were used to construct tables of theoretical data with 0.001 intervals in R_1 . These extended tables are available upon request to the author.

Application to Rate Constant Determinations. For the purpose of demonstrating the use of 2 cycle CV for the determination of rate constants of reactions of electrode generated intermediates two processes which were previously studied extensively and have been evaluated using theoretical data for Mechanisms 1 and 2 were chosen. The system which has been related to data for Mechanism 1 is the protonation of the anthracene anion radical⁶⁻⁸ by phenol (eqns. 1-3) while that corresponding to Mechanism 2 is the dimerization of 9-cyanoanthracene anion radical (eqn. 4) in the presence of acetic acid,⁹ both processes were carried out in *N,N*-dimethylformamide- Bu_4NBF_4 (0.1 M).



Rate constants evaluated from the 2 cycle CV studies are compared to those reported for the two processes under similar conditions in Table 4. The data show that the rate constants evaluated by 2 cycle CV are very close to those reported for

the other techniques. It has previously been pointed out that the rate constants obtained by different techniques for reaction (4) differ slightly.²

Measurement Precision. The standard deviations in R_1 for both processes studied were generally equal to ± 0.001 . For both mechanisms this corresponds to errors in k equal to about $\pm 2\%$. These errors are those to be expected for the measurement of R_1 . In general, the processes studied by transient electrochemical measurements do not afford data which give perfect fit to theoretical working curves for the mechanisms the data are being related to. This imperfect fit of experimental to theoretical data gives rise to additional error, the magnitude of which depends upon the particular system under study. It should be kept in mind that errors of the latter type can be much more serious than those encountered in the measurements.

Conclusions. 2 Cycle CV can provide quantitative electrode kinetic data and is thus a useful addition to the arsenal of transient electrochemical techniques. The precision observed is as good as that for derivative cyclic voltammetry (DCV) and double potential step chronoamperometry (DPSC). The technique is free of some of the limitations previously discussed² for ordinary CV. The data obtained by 2 cycle CV can be used to compliment that from the other methods. Data manipulation which incorporates 1 cycle and 2 cycle CV and DCV from the same experiments should prove to be particularly effective.

Table 3. Polynomial coefficients for theoretical electrode kinetic data for mechanisms 1 and 2.

Coefficient ^a	eCe ₁	eC(dim)
A	0.62461	0.60684
B	-0.11332	-0.099109
C	-0.10001	-0.79639
D	-0.15318	-0.15668
E	-0.063648	-0.072869
F	-0.0075196	-0.0099259

$$^a Y = A + BX + CX^2 + DX^3 + EX^4 + FX^5$$

where Y is R_1

and X is $\log k/a$ for Mechanism 1 or $\log kC/a$ for Mechanism 2.

Table 4. Application of 2 cycle cyclic voltammetry to the study of reaction kinetics.

Process	Technique	$k/\text{M}^{-1} \text{s}^{-1}$	Reference
Protonation of anthracene anion radical by phenol in DMF	2 cycle CV	4800	this work
	DCV	5300	8
	DPSC	4000	8
	DPSC	4500	6
Dimerization of 9-cyanoanthracene anion radical in DMF	DPSC	4800	7
	2 cycle CV	1.47×10^5	this work
	DCV	1.67×10^5	2
	DPSC	1.49×10^5	2
	CV	1.79×10^5	2

Experimental

Reagent grade of anthracene, fluoren-9-one, phenol, and acetic acid were used without further purification. Solutions of Bu_4NBF_4 (0.1 M) in either acetonitrile or *N,N*-dimethylformamide were passed through neutral alumina before use. 9-Cyanoanthracene was the same as used previously.⁹

The cells, electrodes, and instrumentation (with the exception of the function generator noted earlier) were the same as described before.¹⁰ IR compensation was accomplished by adjusting the potentiostat feedback circuit to 85 % of the value where oscillations were observed in the response. This procedure has previously been shown to be adequate with the electrodes and cells used in this study.¹¹

The peak currents were determined by subtracting a baseline current evaluated by a linear regression procedure on 100 data points centered about a potential 250 mV from the peak.

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Received April 26, 1985.