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Cyclic Chronopotentiometry. Systems Involving Kinetic Complications

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ABSTRACT

The extension of cyclic chronopotentiometry to systems involving kinetic complications, including preceding, following, and catalytic reactions and combinations of these is described and tables are given which can be employed in a determination of the rate constants of these reactions. A general digital computer program is presented which allows calculation for any reaction scheme which conforms to the treatment of Ashley and Reilley. Experimental results for the electroreduction of p-nitrosophenol, an ECE-reaction, and the reduction of titanium (IV) in the presence of hydroxylamine, a catalytic reaction, are presented.

The technique of cyclic chronopotentiometry (CC) in which the applied current is successively reversed at each transition and the relative transition times determined, has been applied to simple diffusion controlled reactions (1), multicomponent systems (2), and electrode reactions with following chemical reactions (3). We recently discussed the application of CC to the study of electrode reaction mechanisms (4) and suggested qualitative guides for using CC as a diagnostic aid. We present here a discussion of the methods for solving for the transition time ratios in CC for a number of different reaction schemes involving preceding, following, and intervening chemical reactions and give tables which can be employed in a determination of the rate constants of these reactions. A digital computer program is also described which can be used to determine the relative transition times for any reaction scheme amenable to the treatment of Ashley and Reilley (5).

* Electrochemical Society Active Member.

Theoretical Treatment

One approach which can be employed to compute tables of relative transition times for the different cases involves treatment of each possible reaction scheme separately. Concurrent chemical reactions require additional terms added to Fick's diffusion law. Thus, for the process

$$A_1 \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} A_2 + ne \rightarrow A_3 \qquad k_{32} \qquad [1]$$

the following partial differential equations hold

$$\frac{\partial C_1}{\partial t} = D\frac{\partial^2 C_1}{\partial x^2} - k_{12}C_1 + k_{21}C_2 \qquad [2]$$

$$\frac{\partial C_2}{\partial t} = D\frac{\partial^2 C_2}{\partial x^2} + k_{12}C_1 - k_{21}C_2 + k_{32}C_3 \qquad [3]$$

$$\frac{\partial C_3}{\partial t} = D\frac{\partial^2 C_3}{\partial x^2} - k_{32}C_3 \qquad [4]$$

assuming all diffusion coefficients are equal. C_n is the concentration of the A_n species and the other symbols have their usual meanings. The above system of partial differential equations can be solved by making suitable substitutions, namely $\theta = C_1 + C_2 + C_3$, which gives

$$\frac{\partial \theta}{\partial t} = \frac{D\,\partial^2 \theta}{\partial x^2} \qquad [5]$$

$\gamma = C_3$ which gives

$$\frac{\partial \gamma}{\partial t} = D\frac{\partial^2 \gamma}{\partial x^2} - k\gamma \qquad [6]$$

and $\delta = C_3 + AC_2 + BC_1$, which gives for proper choice of A and B

$$\frac{\partial \delta}{\partial t} = D\frac{\partial^2 \delta}{\partial x^2} - k\delta \qquad [7]$$

Further details concerning the solution of these equations are given by Hung, Delmastro, and Smith (6). Their results for the convolution integral will be used here. For example their solution for the concentrations of A_2 and A_3 for the above case (their equations 78, 79, 109-114 and $k_{CY} = 0$) is the following

$$C_2 = C_2^\circ - [n\mathbf{F}A(D\pi)^{1/2}]^{-1} \left[L_1 \int_0^t e^{-k_{32}\lambda}\, i(t-\lambda)\, \lambda^{-1/2}\, d\lambda \right. \qquad [8]$$

$$\left. - L_2 \int_0^t e^{-(k_{12}+k_{21})\lambda}\, i(t-\lambda)\, \lambda^{-1/2}\, d\lambda \right]$$

$$C_3 = [n\mathbf{F}A(D\pi)^{1/2}]^{-1} \int_0^t e^{-k_{32}\lambda}\, i(t-\lambda)\, \lambda^{-1/2}\, d\lambda \qquad [9]$$

where

$$L_1 = \frac{k_{12} - k_{32}}{k_{12} + k_{21} - k_{32}} \text{ and } L_2 = \frac{k_{21}}{k_{12} + k_{21} - k_{32}}$$

Substitution of constant current boundary conditions and proper use of the step function theorem allows solution for the CC transition time ratios. The procedure is quite similar to the method used in earlier papers in this series where the computer programs were published (1-3).

In this case the computer program would generate the following equation for the third transition time

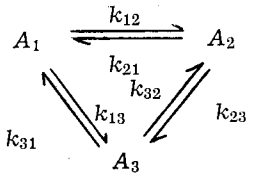
$$f(x) = k_{21}(k_{12} + k_{21})^{-1/2}[erf(\{(k_{12} + k_{21})x\}^{1/2})] + (k_{12} - k_{32})(k_{32})^{-1/2}[erf(\{k_{32}x\}^{1/2})] \qquad [10]$$

and

$$f(\tau_1) = f(\tau_1 + \tau_2 + \tau_3) - Rf(\tau_2 + \tau_3) + Rf(\tau_3) \qquad [11]$$

where τ_1 is one, $erf(x) = 2\pi^{-1/2}\int_0^x e^{-\tau^2}\, d\tau$, $R = (i_{Red} + i_{ox})/i_{Red}$ and τ_2 is calculated in the previous step from an equation representing A_2. The above nonlinear equation is solved using a standard numerical technique, *e.g.*, the Newton-Raphsen method. Successive approximations are generated from evaluations of the function and its derivative. Occasionally this method does not converge and it is necessary to use our previous "brute force" method (1) which is quite a bit slower. While this approach works well and extensive tables of transition time ratios can be prepared in a comparatively short time using a digital computer, certain statements in the program have to be drastically modified each time a different mechanism is considered. Most of the theoretical calculations reported here were done using the above method and the convolution integrals reported by Hung, Delmastro, and Smith (6).

Recently Ashley and Reilley (5) showed how electrochemical systems coupled only by first order chemical reactions could be treated in a general way and general equations formulated. They considered subsystems of the form



[12]

and obtained the following equation for the concentration of the species in the Laplace transform plane

$$\bar{C}_n = \bar{C}_n^0 - D^{-1/2} \sum_g \bar{i}_g \sum_h K_{fgh}\, (s + \chi_h)^{-1/2} \qquad [13]$$

where K_{fgh} and χ_h are constants, which are determined by the rate constants of the coupled reactions in [12]. This equation is derived using substitutions such as those described before and applying matrix algebraic methods. The values of K_{fgh} and χ_h in terms of the rate constants are given in (5). Inverse transformation of [13] gives the desired convolution integral. This is particularly easy for chronopotentiometry, because the fluxes of the components are constant.

The computer program discussed before was modified to treat the more general case embodied by Eq. [13]. A FORTRAN subroutine was written which evaluated the constants K_{fgh} and χ_h and FORTRAN function subprograms were used to evaluate the summation and its derivative. The Newton-Raphsen method could then be used to solve for the individual transition time ratios. As expected, both methods gave the same results for selected systems. However, the general method is by far the more convenient. It is just necessary to label the species in a subsystem, decide which are oxidized or reduced and what values should be picked for the rate constants and the program does the rest. The only programming changes which are necessary when different reaction schemes are considered involve only input and output. A listing of this program for the system in Eq. [12] is available to interested readers and can easily be adapted to other mechanisms.

Theoretical Results

The characteristics of each mechanism are treated separately. The mechanisms that are discussed include reversible chemical reactions preceding, following, and in parallel (catalytic), with the electrode process proper, as well as mixtures of each. The convolution integrals have been tabulated by Smith and coworkers (6) and will not be repeated. The familiar ECE case and its extension is also discussed. For all of the cases described we assume an initial reduction, equal diffusion coefficients for all species, and equal current densities for reduction and oxidation.

Table I. Relative transition times for cyclic chronopotentiometry with a preceding chemical reaction

$$A_1 \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} A_2 + ne \rightarrow A_3$$

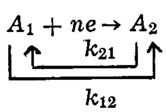
n	a_n								
$k_{12}\tau_1$ =	0.5	0.5	0.5	1.0	1.0	1.0	2.0	2.0	2.0
$k_{21}\tau_1$ =	0.5	1.0	2.0	0.5	1.0	2.0	0.5	1.0	2.0
1	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
2	0.333	0.333	0.333	0.333	0.333	0.333	0.333	0.333	0.333
3	0.684	0.733	0.750	0.641	0.665	0.670	0.606	0.614	0.614
4	0.392	0.411	0.417	0.375	0.385	0.387	0.362	0.365	0.365
5	0.670	0.721	0.725	0.607	0.631	0.633	0.565	0.573	0.573
6	0.428	0.455	0.458	0.397	0.410	0.411	0.376	0.380	0.380
7	0.663	0.713	0.711	0.590	0.614	0.615	0.545	0.553	0.554
8	0.452	0.483	0.483	0.411	0.426	0.426	0.385	0.389	0.390
9	0.659	0.707	0.702	0.579	0.603	0.604	0.533	0.541	0.542
10	0.469	0.502	0.500	0.420	0.436	0.437	0.391	0.396	0.397

Preceding chemical reaction.—

$$A_1 \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} A_2 + ne \rightarrow A_3 \qquad [14]$$

Relative transition times ($a_n = \tau_n/\tau_1$) for this case for different values of k_{12} and k_{21} are given in Table I. Note that in this case the second relative transition time (a_2) is not affected by the chemical reaction, but a_3 becomes larger than in the diffusion controlled case. In most cases the odd relative transition time decreases as in the diffusion case, but if the rate of the reverse reaction ($k_{21}\tau_1$) is large, increases may be observed. If both values of the rate constant are quite large the diffusion controlled situation is approached again. This is true of many of the reversible mechanisms. A preceding chemical reaction can be positively differentiated from a catalytic type mechanism in which τ_3 may be larger than diffusion by its diffusion controlled value of a_2 (1/3). In some of the reversible cases a steady state value for the relative transition times may be attained which can be used to calculate the rate constants, although convection might interfere with this measurement.

Parallel (catalytic) reversible reaction.—



[15]

The case of CC involving an irreversible catalytic reaction has been treated previously (3); we extend the work here to include a reversible reaction (Table II). Since A_1 and A_2 are in equilibrium before the application of the constant current, it is possible for the second transition time to be larger than the first. Any reaction involving a reversible catalytic system can be identified by the fact that an equilibrium amount of reduced form is present. Initial oxidations can confirm this presence. The second transition time may be lower than the diffusion controlled value but the third is higher than would be expected from an irreversible catalytic or kinetic mechanism calculated for the same rate constant. Interestingly we have found empirically that no second transition can be calculated for values of the rate constants when

$$(k_{12}/k_{21})\ erf\{(k_{12}\tau_1)^{1/2}\} \geqq 1$$

Following reversible reaction.—

$$A_1 + ne \rightarrow A_2 \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} A_3 \qquad [16]$$

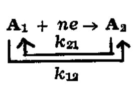
This case, treated previously for an irreversible following reaction [3], is characterized (Table III) by a second relative transition time which is smaller than 0.333. The even relative transition times calculated assuming this mechanism do not decay as fast as those found for an irreversible following reaction. No initial concentration of A_2 would normally be observed with this system.

ECE mechanism.—

$$A_1 + ne \rightarrow A_2 \overset{k_{23}}{\rightarrow} A_3 + ne \rightarrow A_4 \qquad [17]$$

This reaction sequence is fundamentally different from the general sequence of Eq. [12], and cannot be treated by modification of the general computer program for a three component subsystem. The ECE mechanism under consideration here is the one in which A_3 is reduced at potentials considerably less cathodic than those required to reduce A_1, so that on current reversal where A_2 is oxidized, A_3 continues to reduce. The treatment involves evaluating the cur-

Table II. Relative transition times for cyclic chronopotentiometry with a parallel (catalytic) reaction



n	a_n				
$k_{12}\tau_1$ =	0.5	0.5	1.0[a]	0.0	0.0
$k_{21}\tau_1$ =	0.5	1.0	1.0	0.5	1.0
1	1.000	1.000	1.000	1.000	1.000
2	1.414	0.370	1.273	0.227	0.167
3	1.408	1.035	1.272	0.634	0.673
4	1.409	0.370	1.272	0.232	0.169
5	1.409	1.033	1.272	0.609	0.658
6	1.409	0.370	1.272	0.233	0.169
7	1.409	1.033	1.272	0.600	0.655
8	1.409	0.370	1.272	0.234	0.169
9	1.409	1.033	1.272	0.597	0.654
10	1.409	0.370	1.272	0.234	0.169

[a] No reverse transition is observed for $k_{12}\tau_1 = 1.0$ and $k_{21}\tau_1 = 0.5$.

Table III. Relative transition times for cyclic chronopotentiometry with a following reaction

$$A_1 + ne \rightarrow A_2 \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} A_3$$

n	a_n					
$k_{23}\tau_1$ =	0.5	1.0	0.5	1.0	0.5	1.0
$k_{32}\tau_1$ =	0.0	0.0	0.5	0.5	1.0	1.0
1	1.000	1.000	1.000	1.000	1.000	1.000
2	0.227	0.167	0.244	0.188	0.258	0.207
3	0.463	0.384	0.484	0.413	0.501	0.438
4	0.200	0.138	0.233	0.171	0.258	0.201
5	0.373	0.292	0.412	0.336	0.441	0.373
6	0.180	0.120	0.226	0.162	0.259	0.198
7	0.321	0.243	0.375	0.298	0.412	0.342
8	0.165	0.108	0.222	0.156	0.260	0.197
9	0.285	0.211	0.351	0.274	0.394	0.323
10	0.153	0.099	0.218	0.152	0.261	0.196

rent transforms of A_1 and A_2 by the method described in detail in a previous paper (7). The relative transition times are determined in the same manner as before, after inverse transformation of the concentration response (Table IV).

Several recent communications have discussed methods of treating the ECE mechanism [see ref. (7-10) and references contained therein]. An ECE reaction is indicated when another electrode couple appears at potentials less cathodic than those of the main reduction wave. The third transition time, although smaller than that observed in a diffusion controlled reaction, is not as small as that of an irreversible following reaction.

Hawley and Feldberg (8) recently pointed out that for the ECE mechanism treated above, the following additional reaction should be considered

$$A_2 + A_3 \rightleftharpoons A_1 + A_4 \qquad [18]$$

A preliminary investigation of relative transition times taking account of this reaction shows only very small differences with transition times in Table IV, so that CC is probably not useful in gauging the importance of [18] in a proposed ECE mechanism.

Mixtures of the above cases.—A large number of possible reaction schemes can result from the simultaneous occurrence of preceding, parallel, and following reactions. Some typical cases are shown in Table V. In general these more complicated cases are suggested when relative transition time trends similar to the simpler cases are observed, but a good fit to these simpler cases cannot be obtained with a given set of rate constants. However, as more complicated schemes are invoked to explain a reaction, more and more adjustable parameters (rate constants) are included and a better fit to the experimental data is expected. CC has the advantage over cyclic voltammetry that the rate constants of the electron transfer reactions do not enter into the consideration, but CC is probably more sensitive to adsorption of reactants, products, and intermediates. Certainly elucidation of a reaction mechanism requires that other electrochemical techniques, such as polarography and coulometry, and analysis of reaction products and intermediates, also be undertaken.

Experimental Results

Electroreduction of p-nitrosophenol.—The electroreduction of p-nitrosophenol has been studied by various workers (7, 10, 11) using a variety of techniques and has been shown to follow the general ECE reaction scheme. The following reactions are given for the reaction

$$NO-C_6H_4-OH + 2H^+ + 2e \rightarrow \overset{H}{HON}-C_6H_4-OH \qquad [19]$$

$$\overset{H}{HON}-C_6H_4-OH \xrightarrow{k} HN=C_6H_4=O + H_2O \qquad [20]$$

$$HN=C_6H_4=O + 2H^+ + 2e \rightarrow H_2N-C_6H_4-OH \qquad [21]$$

A comparison of experimental results for the relative transition times in CC with calculated ones are given in Table VI. We also considered the possibility of the following reaction occurring in the reaction sequence, after the suggestion of Hawley and Feldberg (8)

$$HOH-C_6H_4-OH + HN=C_6H_4=O \xrightarrow{\text{fast}} H_2N-C_6H_4-OH + NO-C_6H_4-OH \qquad [22]$$

If the rate of Eq. [22] is assumed fast, calculated results assuming the sequence Eq. [19], [20], [22] fit the experimental data just as well as with an assumed ECE mechanism. The rate constant for Eq. [20] by either mechanism is about the same. This finding is in agreement with that for chronoamperometry (8) where it was found that for small values of kt (or in CC, small values of $k\tau_1$) both mechanisms give almost the same working curves. Note that it is relatively easy to differentiate the ECE mechanism from other common possibilities with the use of cyclic chronopotentiometry. The decrease in the second relative transition time could be explained by a simple catalytic or kinetic mechanism. The 3rd transition time (and subsequent ones) serves to differentiate among these mechanisms.

Electroreduction of titanium (IV)—hydroxylamine system.—The reaction of electrochemically generated titanium (III) with hydroxylamine has been studied by several groups (3, 12-14). In a previous study in this series (3) we used this reaction as an example of a simple catalytic reaction scheme, *i.e.*

$$A_1 + ne \rightarrow A_2 \qquad [23]$$

$$A_2 + Y \xrightarrow{k} A_1 \qquad [24]$$

Some discrepancy was found between the theoretical calculations and the experimental results for that system. The experiments were done under conditions where the pseudo first-order rate constant (kC_Y) had to be low because of the limitations imposed by the use of mechanical relays for switching. Because the hydroxylamine concentration had to be kept small, the ratio of hydroxylamine to titanium (IV) was only about 25 to 1. This may not have been a sufficient excess of reactant to maintain true pseudo first-order conditions. The experiments were repeated here using the electronic switching apparatus previously described (15) and ratios of hydroxylamine to titanium (IV) of 200 to 1. The relative transition times found under these conditions are in much better agreement with the simple catalytic mechanism than those given before (Table VII). The rate constant calculated from this data is also in good agreement with that reported by Christie and Lauer (12) at the concentration ratio. Further studies on this system to determine the range of pseudo first-order conditions is presently under investigation by one of us (HBH). Since this system does not give very well-defined complete chronopotentiograms, cyclic chronopotentiometry would probably not be the method of choice in an experimental study. Poor forward transitions are usually found for catalytic systems so that a method such as current reversal chronopotentiometry, which does not require going through a first transition, would be more suitable.

Table IV. Relative transition times for cyclic chronopotentiometry with ECE mechanism

$$A_1 + ne \rightarrow A_2 \xrightarrow{k_{23}} \underset{a_n}{A_3} + ne \rightarrow A_4$$

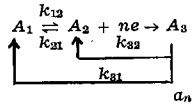
n	$k_{23}\tau_1 =$ 0	0.2	0.4	0.6	0.8	1.0
1	1.000	1.000	1.000	1.000	1.000	1.000
2	0.333	0.241	0.182	0.142	0.114	0.093
3	0.588	0.542	0.494	0.447	0.403	0.362
4	0.355	0.228	0.161	0.120	0.094	0.076
5	0.546	0.471	0.406	0.352	0.306	0.269
6	0.366	0.215	0.145	0.106	0.082	0.066
7	0.525	0.427	0.353	0.297	0.254	0.220
8	0.373	0.203	0.133	0.096	0.074	0.060
9	0.513	0.394	0.315	0.260	0.220	0.190
10	0.378	0.192	0.123	0.089	0.068	0.055

Conclusion

Cyclic chronopotentiometry does appear to have some real advantages for study of complicated reactions over other techniques. Since the general solution for coupled chemical reactions in a three component subsystem has appeared (3), the method presented here can be used to prepare tables of transition times ratios for the systems discussed and many other possible reaction schemes. No assumptions are required about the rates of electron transfer, which complicate considerations in other techniques, such as cyclic volt-

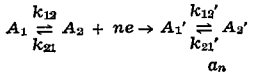
Table V. Relative transition times for cyclic chronopotentiometry for several reaction schemes

1. Reversible preceding with irreversible catalytic reaction



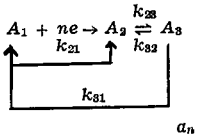
n	$k_{31}\tau_1 =$	—	—	—	—	—	—	—	0.5	1.0
	$k_{12}\tau_1 =$	0.5	0.5	1.0	1.0	0.5	1.0	1.0	0.5	1.0
	$k_{21}\tau_1 =$	0.5	1.0	1.0	0.5	0.5	1.0	0.5	0.5	1.0
	$k_{32}\tau_1 =$	0.5	0.5	0.5	0.5	1.0	1.0	1.0	0.5	1.0
1		1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
2		0.227	0.227	0.227	0.227	0.167	0.167	0.167	0.167	0.105
3		0.777	0.881	0.748	0.708	0.673	0.867	0.785	0.673	0.737
4		0.254	0.268	0.250	0.244	0.169	0.182	0.177	0.169	0.105
5		0.805	0.931	0.739	0.698	0.658	0.889	0.796	0.658	0.733
6		0.267	0.286	0.257	0.250	0.169	0.186	0.180	0.169	0.105
7		0.823	0.952	0.735	0.693	0.655	0.895	0.801	0.655	0.732
8		0.274	0.294	0.260	0.252	0.169	0.187	0.181	0.169	0.105
9		0.833	0.960	0.734	0.692	0.654	0.896	0.803	0.654	0.732
10		0.277	0.297	0.261	0.253	0.169	0.187	0.181	0.169	0.105

2. Reversible preceding with following reaction



n	$k_{21}'\tau_1 =$	—	—	—	—	—	—	—	—	0.5	1.0
	$k_{12}\tau_1 =$	0.5	0.5	1.0	1.0	0.5	0.5	1.0	1.0	0.5	1.0
	$k_{21}\tau_1 =$	0.5	1.0	1.0	0.5	0.5	1.0	1.0	0.5	0.5	1.0
	$k_{12}'\tau_1 =$	0.5	0.5	0.5	0.5	1.0	1.0	1.0	1.0	0.5	1.0
1		1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
2		0.227	0.227	0.227	0.227	0.167	0.167	0.167	0.167	0.244	0.207
3		0.555	0.611	0.547	0.517	0.468	0.527	0.469	0.436	0.577	0.522
4		0.218	0.228	0.217	0.211	0.149	0.155	0.149	0.145	0.256	0.219
5		0.477	0.536	0.460	0.430	0.380	0.438	0.373	0.342	0.524	0.462
6		0.206	0.220	0.202	0.195	0.136	0.145	0.135	0.130	0.264	0.227
7		0.427	0.484	0.405	0.376	0.330	0.384	0.319	0.290	0.495	0.431
8		0.195	0.210	0.190	0.182	0.127	0.136	0.124	0.119	0.269	0.232
9		0.389	0.444	0.366	0.338	0.296	0.347	0.282	0.256	0.476	0.413
10		0.185	0.200	0.179	0.170	0.119	0.129	0.116	0.110	0.274	0.237

3. Reversible following with catalytic reaction



n	$k_{31}\tau_1 =$	—	—	—	—	—	—	—	0.5	1.0
	$k_{32}\tau_1 =$	0.5	0.5	1.0	1.0	0.5	1.0	1.0	0.5	1.0
	$k_{23}\tau_1 =$	0.5	1.0	1.0	0.5	0.5	1.0	0.5	0.5	1.0
	$k_{21}\tau_1 =$	0.5	0.5	0.5	0.5	1.0	1.0	1.0	0.5	1.0
1		1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
2		0.177	0.143	0.155	0.185	0.136	0.122	0.141	0.176	0.118
3		0.497	0.414	0.445	0.520	0.500	0.445	0.530	0.549	0.563
4		0.168	0.131	0.149	0.182	0.129	0.117	0.138	0.171	0.116
5		0.430	0.341	0.385	0.468	0.434	0.389	0.481	0.505	0.537
6		0.162	0.124	0.146	0.180	0.125	0.114	0.136	0.168	0.116
7		0.396	0.305	0.358	0.445	0.402	0.365	0.461	0.487	0.530
8		0.158	0.120	0.144	0.179	0.122	0.113	0.135	0.167	0.115
9		0.376	0.284	0.343	0.432	0.382	0.351	0.450	0.479	0.528
10		0.156	0.117	0.144	0.179	0.121	0.113	0.135	0.166	0.115

ammetry. The data for CC can be interpreted without knowing the applied current, electrode area, diffusion coefficient, or concentration. It is sufficient to measure the relative transition time ratios and the first transition time in order to calculate the chemical rate constants, if the mechanism is known. If the mechanism is not known, CC can be used as a diagnostic tool to eliminate all but a few plausible reactions.

Cyclic chronopotentiometry does appear to have some real disadvantages. The effect of double layer charging and of adsorption of electroactive species has been ignored. Both tend to reduce the fraction of the current (ideally one) which goes to the faradaic reaction. Ordinary CC can be improved by the addition of derivative readout and some work along these lines has been reported (16).

Experimental

The operational amplifier apparatus previously described (15) was used for cyclic chronopotentiometry. The p-nitrosophenol was purified according to the directions of Alberts and Shain (11). Fischer purified titanium tetrachloride was used as-received. The potential-time curves were recorded on a Tektronix 564 storage oscilloscope and photographed with a Tektronix C27 oscilloscope camera equipped with a Polaroid back.

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1969 JOURNAL.

Table VI. Experimental and theoretical relative transition times for electroreduction of p-nitrosophenol[a]

	a_n	
n	Experimental	Theoretical
1. τ_1 = 1.34 sec. Theoretical calculated for $k\tau_1$ = 0.56 (k = 0.42 sec^{-1})		
1	1.000	1.000
2	0.149	0.149
3	0.449	0.457
4	0.136	0.127
5	0.372	0.362
6	0.121	0.112
2. τ_1 = 0.655 sec. Theoretical calculated for $k\tau_1$ = 0.26 (k = 0.40 sec^{-1})		
1	1.000	1.000
2	0.220	0.220
3	0.527	0.528
4	0.198	0.204
5	0.458	0.450
6	0.186	0.189

[a] Solution contained 1.0 mM p-nitrosophenol in a buffer of 1.0M acetic acid, 1.0M sodium acetate, and 1.0M potassium nitrate (20% v/v) ethanol). Hanging mercury drop electrode employed.

Table VII. Experimental and theoretical relative transition times for electroreduction of titanium (IV) in the absence and presence of hydroxylamine[a]

$$\text{Ti (IV)} + e \rightarrow \text{Ti (III)}$$
$$\uparrow_{k\ \ NH_2OH}$$

	a_n	
n	Experimental	Theoretical
1. No hydroxylamine; io = 0.43 ma/cm^2; τ = 180 msec		
1	1.00	1.00
2	0.34	0.33
3	0.62	0.59
4	0.34	0.36
5	0.58	0.55
6	0.36	0.37
2. 0.20M hydroxylamine; io = 0.74 ma/cm^2; τ_1 = 86 msec. Theoretical calculated for $kC\ \tau_1$ = 0.70 (k = 40 l-mole^{-1}-sec^{-1})[b]		
1	1.00	1.00
2	0.20	0.20
3	0.67	0.65
4	0.24	0.20
5	0.66	0.63
6	0.23	0.20

[a] Solution contained 1.0 mM titanium (IV) and 0.20M $H_2C_2O_4$. Hanging mercury drop electrode employed.
[b] Compare to k = 37 [ref. (12)], k = 45 (polarography), and k = 33 (from first transition time) l-mole^{-1}-sec^{-1}.

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