Cyclic Chronopotentiometry

Electron Transfer with Following Chemical Reaction

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▶ The application of cyclic chrono-potentiometry to the study of an electrode reaction followed by an irreversible pseudo-first-order chemical reaction of the product is considered. Discussed are reactions leading to the production of a nonelectroactive species, regeneration of the original electroactive species, or both simultaneously; equations for the successive transition times are derived and solved. The oxidation of p-aminophenol and the reduction of titanium(IV) in the presence of hydroxylamine have been examined experimentally by this technique. A circuit for automatic measurement of the successive transition times is described.

CYCLIC chronopotentiometry (CC) is a technique in which the applied current is successively reversed at each transition. In a previous communication (5) the technique was introduced and theoretical equations for the diffusion controlled electrode reaction of a single component system were derived and verified. The present paper is concerned with CC in systems in which a first or pseudo-first-order chemical reaction follows the electrode reaction. In all cases the electrode reaction is given by

$$O + ne \rightarrow R \quad (1)$$

where O is the original electroactive species and R is the product of the electrode reaction. The following chemical reactions are considered:

1. Kinetic case

$$R \xrightarrow{k} Y \quad (2)$$

2. Catalytic case

$$R \xrightarrow{k} O \quad (3)$$

3. Kinetic–catalytic case

$$R \xrightarrow{k_1} O \quad (4)$$

$$R \xrightarrow{k_2} Y \quad (5)$$

where Y is not electroactive in the potential range of interest. For each case the theoretical equations, based on

current impulse response functions (5, 6), have been derived and these equations solved for the relative transition times.

EXPERIMENTAL

The basic instrumentation for CC has been described (5). The mercury pool and platinum electrodes were shielded for linear diffusion. The current was reversed automatically at present potentials and the potential-time curve recorded. To record the transition times directly, the auxiliary circuit (Figure 1) was also used.

The operation of this circuit is based upon a digital counter (Hewlett Packard Model 522B) and recorder (Hewlett Packard Model 560A). When the counter is used in the Time Interval mode, a voltage pulse into the trigger input will start the counter counting an internal standard frequency. Another voltage pulse terminates the count. The voltage pulses were derived from auxiliary contacts of relays RL 1 and RL 5 in the circuit previously given (5). Several minor modifications were made in this circuit. An additional 5.6 K resistor was added to the plate circuit of V 2 to make the action of RL 5 truly momentary. The latching circuit was changed by adding a 4.7 K resistor in series with the relay coils, by increasing the battery voltage to 100 volts, and by allowing RL 5 to short the coils of RL 2, 3, and 4 rather than just interrupt the current through these coils. These changes were made to ensure that the contacts of RL 5 connected with the opposite contacts before reverting to the normal position. The counter has a minimum display time of about 0.1 second and the digital recorder requires about 0.15 second for its printing wheels to position and lock. Therefore, to record successive transition times, a simple R-C circuit which delays the start count pulse about 0.15 second after the preceding stop pulse, was added. This delay was quite constant and transition times could be corrected by adding 0.15 second to the printed values.

The operation of the circuit is as follows. The DPDT switch that starts the electrolysis, S 1, also closes the circuit that charges the capacitor connected to the trigger input of the counter. When the voltage across the capacitor reaches about 30 volts, the counter starts. At the first transition the contacts of RL 1 close, shorting the

capacitor; the count stops immediately and the digital recorder prints the first transition time. Since the action of RL 1 is momentary, the contacts open immediately and the capacitor begins to charge again and at 30 volts the count begins again. At the second transition RL 5 closes momentarily, causing the second transition time to be printed. This procedure is repeated each time RL 1 or RL 5 closes. Typical settings on the H.P. 522 B counter are: function selector—time interval; time unit—seconds; trigger input—common; trigger level start—30 volts, stop—0 volts; trigger slope start—negative, stop—positive; and display time set at minimum.

This circuit is also useful for measuring single transition times with the delay circuit removed by shorting the 220 K resistor. Single transition times down to 100 millisec. were measured using this automatic circuit. Relative transition times for CC were determined using the automatic circuit described and from strip chart recorder measurements.

THEORETICAL

Theoretical equations for the relative transition times in CC with kinetic complications were derived by extending the "response function additivity" principle of Murray and Reilley (6). Although the derivations will be given for an initial reduction followed by reversals of current, the final results apply equally well to an initial oxidation. Species R is assumed absent initially.

Case 1. Kinetic Case. The case of a single irreversible chemical reaction (2) removing R following the electrode reactions has been treated by several authors for single and multiple current reversals (2, 9). Convenient forms of equations for solving this problem can be obtained from those by Smith (8) (Equation 59), assuming the back chemical reaction rate is negligible:

$$C_O(0, t) = C_O{}^\circ - [nF(\pi D_O)^{1/2}]^{-1} \int_0^t i(t - \lambda)\lambda^{-1/2}d\lambda \quad (6)$$

$$C_R(0, t) = [nF(\pi D_R)^{1/2}]^{-1} \int_0^t e^{-k\lambda} i(t - \lambda)\lambda^{-1/2}d\lambda \quad (7)$$

where $C_O{}^\circ$ is the initial concentration of species O, $C_O(0, t)$ and $C_R(0, t)$ are

Figure 1. Schematic diagram for automatic printing circuit

RL 1 and RL 5 refer to relays in previously published circuit (5)

Figure 2. Cyclic chronopotentiogram for oxidation of p-aminophenol

Solution contained 1.14mM p-aminophenol in 0.1M H₂SO₄. Current density was 0.271 ma. per sq. cm. at platinum disk electrode

the concentrations of O and R at the electrode surface at time t, $i(t - \lambda)$ is the current density, which may be a function of time, λ is a dummy variable of integration, k is the rate constant of reaction 2, and the other symbols have their usual meanings. Following the procedure outlined for CC with diffusion controlled reaction [Appendix I in (5)] the following equations are obtained:

$$nFD_0^{1/2}[C_0^\circ - C_0(0, t)] = \sum_p Z_p(0, t - t_p) \quad (8)$$

$$Z_p = \pi^{-1/2} \int_0^{t - t_p} i_p(t - \lambda)\lambda^{-1/2}d\lambda \quad (9)$$

$$nFD_R^{1/2}C_R(0, t) = \sum_p Z_p '(0, t - t_p) \quad (10)$$

$$Z_p' = \pi^{-1/2} \int_0^{t - t_p} e^{-k\lambda} i_p(t - \lambda) \lambda^{-1/2}d\lambda \quad (11)$$

where Z_p and Z_p' are the current impulse response functions for species O (5, 6) and species R, respectively. Z_p is the usual diffusion controlled function, while Z_p' also takes account of the chemical reaction.

For a constant current density, i_{Red}, Equation 9 is evaluated as before (5) and Equation 11 is evaluated by substituting $\theta = (k\lambda)^{1/2}$. At the first transition time, τ_1, and all successive odd-numbered transitions (reductions), $C_0(0, t)$ is zero, and Equation 8 becomes:

$$\frac{nF(\pi D_0)^{1/2}C_0^\circ}{2 i_{Red}} = (\tau_1 + \tau_2 + \ldots \tau_n)^{1/2} - R(\tau_2 + \ldots \tau_n)^{1/2} + \ldots R(\tau_n)^{1/2} \quad (12)$$

For even-numbered transitions (oxidations), $C_R(0, t)$ is zero, and from Equation 11

$$0 = erf [k(\tau_1 + \tau_2 + \ldots \tau_n)]^{1/2} - R erf [k(\tau_2 + \ldots \tau_n)]^{1/2} + \ldots R erf (k\tau_n)^{1/2} \quad (13)$$

$$R = \frac{i_{Ox} + i_{Red}}{i_{Red}} \quad (14)$$

For equal anodic and cathodic current densities, R is 2. The first transition time, τ_1, is unaffected by the chemical reaction. However, τ_2 is shorter than

the corresponding τ_2 for a diffusion controlled reaction; the extent of decrease in τ_2 depends upon the product of the rate constant, k and τ_1.

Equations 12 and 13 were generated and solved for different values of $k\tau_1$ using a digital computer. The Fortran program used is given in the appendix. Calculated relative transition times, a_n's (where $a_n = \tau_n/\tau_1$) for various values of $k\tau_1$ are given in Table I. Note that the relative transition times for all $n \geq 2$ are smaller than those in the diffusion controlled case because of removal of the product R by the chemical reaction.

Case 2. Catalytic Case. Chronopotentiometry with a single, irreversible reaction regenerating the electroactive species (3) has been treated for the first transition and for a single reversal (3, 4). The current impulse response functions can be obtained from equations for O and R given by Smith (8, Equations 73 and 74).

$$C_0(0, t) = C_0^\circ - [nF(\pi D_0)^{1/2}]^{-1} \int_0^t e^{-k\lambda} i(t - \lambda)\lambda^{-1/2}d\lambda \quad (15)$$

$$C_R(0, t) = [nF(\pi D_R)^{1/2}]^{-1} \int_0^t e^{-k\lambda} i(t - \lambda)\lambda^{-1/2}d\lambda \quad (16)$$

Following the method given under Case 1, the following current impulse response function is obtained

$$Z_p' = \pi^{-1/2} \int_0^{t - t_p} e^{-k\lambda} i_p(t - \lambda)\lambda^{-1/2}d\lambda \quad (17)$$

for both oxidations and reductions. Assuming constant current densities, evaluating Equation 17 as before, and combining with Equations 8 and 10 yield the following equations for the transition times.

Even-numbered transition times (reductions):

$$\frac{nF(kD_0)^{1/2}C_0^\circ}{i_{Red}} = erf [k(\tau_1 + \tau_2 + \ldots \tau_n)]^{1/2} - R erf [k(\tau_2 + \ldots \tau_n)]^{1/2} + \ldots R erf [k\tau_n]^{1/2} \quad (18)$$

Odd - numbered transition time (oxidations):

$$0 = erf [k(\tau_1 + \tau_2 + \ldots \tau_n)]^{1/2} - R erf [k(\tau_2 + \ldots \tau_n)]^{1/2} + \ldots R erf [k\tau_n]^{1/2} \quad (19)$$

Equations 17 and 18 were generated and solved for the various transition times at different values of $k\tau_1$ using the digital computer program in the appendix. Calculated relative transition times are given in Table I. Note that a_2 is smaller than in the diffusion-controlled case, but a_3 is larger because O is regenerated. For repeated reversals, all odd-numbered transitions are longer and all even-numbered transitions are shorter than in the corresponding diffusion-controlled case.

Case 3. Kinetic-Catalytic Case. The case for chronopotentiometry for both a kinetic (4) and a catalytic (5) chemical reaction following the electrode reaction was considered only for the first transition by Sartori, Furlani, and Morpurgo (7). The system is described by the following equations:

$$C_0(0, t) = C_0^\circ - [nF(\pi D_0)^{1/2}(k_1 + k_2)]^{-1} \left[k_1 \int_0^t e^{-(k_1 + k_2)\lambda} i(t - \lambda)\lambda^{-1/2}d\lambda + k_2 \int_0^t i(t - \lambda)\lambda^{-1/2}d\lambda \right] \quad (20)$$

$$C_R(0, t) = [nF(\pi D_R)^{1/2}]^{-1} \int_0^t e^{-(k_1 + k_2)\lambda} i(t - \lambda)\lambda^{-1/2}d\lambda \quad (21)$$

Following the procedure outlined under Case 1, the following response function is obtained for species O:

$$Z_p' = [\pi^{1/2}(k_1 + k_2)]^{-1} \left[k_1 \int_0^{t - t_p} e^{-(k_1 + k_2)\lambda} i_p(t - \lambda)\lambda^{-1/2}d\lambda + k_2 \int_0^{t - t_p} i_p(t - \lambda)\lambda^{-1/2}d\lambda \right] \quad (22)$$

The response function for species R is given by Equation 17, with k replaced by $(k_1 + k_2)$. Evaluating Equation 22 for constant current den-

sities and combining with Equation 8 yield for odd-numbered transitions:

$$\frac{nF(D_O\pi)^{1/2}C_O{}^\circ}{i_{Red}} =$$

$$\frac{2k_2}{(k_1 + k_2)} [(\tau_1 + \tau_2 + \dots \tau_n)^{1/2} -$$

$$R(\tau_2 + \dots \tau_n)^{1/2} + \dots R\tau_n{}^{1/2}] +$$

$$\frac{k_1\pi^{1/2}}{(k_1 + k_2)^{3/2}} [erf [(k_1 + k_2) (\tau_1 + \tau_2 +$$

$$\dots \tau_n)]^{1/2} - R \; erf \; [(k_1 + k_2) (\tau_2 +$$

$$\dots \tau_n)]^{1/2} + \dots R \; erf \; [(k_1 + k_2)\tau_n]^{1/2}]$$

$$(23)$$

Even-numbered transitions are given by Equation 19, with k replaced by $(k_1 + k_2)$.

The equations describing the system were solved using the program in the appendix, and typical results are given in Table I. The relative transition time magnitudes depend upon the relative size of the two rate constants, and approach Case 1 and Case 2 as the ratio k_1/k_2 approaches zero and infinity, respectively. For intermediate values of k_1/k_2, a_3 may either be larger or smaller than the value of a_2 found in the catalytic or kinetic cases alone. In all cases the even-numbered relative transition times are smaller than for the diffusion-controlled case, and continually decrease.

RESULTS AND DISCUSSION

The theoretical equations for Case 1, involving a secondary chemical reaction, were tested by studying the CC of p-aminophenol (PAP) at a platinum electrode. The oxidation of PAP has been studied by several workers [see (9) and references contained therein] and has been shown to follow the following reaction scheme in dilute H_2SO_4:

$$HO—C_6H_4—NH_2 - 2e \rightleftarrows$$
$$O=C_6H_4=NH + 2H^+ \quad (24)$$

$$O=C_6H_4=NH + H_2O \xrightarrow{k}$$
$$O=C_6H_4=O + NH_3 \quad (25)$$

On current reversal, the imine is reduced, and at a more negative potential, the benzoquinone is reduced. When the potential limits are set so that only the oxidation of PAP and the reduction of the imine occur, the system follows Case 1. A typical cyclic chronopotentiogram of PAP in 0.10M H_2SO_4 is shown in Figure 2. The first wave,

Figure 3. Theoretical and experimental relative transition times for cyclic chronopotentiometry with following chemical reaction (Case 1)

- - - Theoretical for $k\tau_1 = 0.75$
O O O Experimental, for oxidation of p-aminophenol at 24.5° C.

and all subsequent odd-numbered waves, involve the oxidation of PAP, Reaction 24. The first reversal, and all subsequent even-numbered waves, involve the reduction of the imine; the benzoquinone is not electroactive in this potential range.

Tables of relative transition times for various values of $k\tau_1$ were computed using the program in the appendix. Experimental relative transition times were compared to those in the tables and the rate constant was determined. Alternately, the experimental data could be used to evaluate the rate constant directly, using a slight modification of the listed program. A comparison of the experimental relative transition times with those calculated for a $k\tau_1$ of 0.75 is shown in Figure 3. The pseudo-first-order rate constant was calculated to be 0.086 and 0.115 sec.$^{-1}$ at 24.5° and 30° C., respectively, in good agreement with the value of 0.103 sec.$^{-1}$ obtained by Testa and Reinmuth (9) at 30° C. using single current reversal chronopotentiometry.

When the cathodic potential limit is set at a more negative potential, the following reaction can also occur:

$$O=C_6H_4=O + 2H^+ + 2e \rightarrow$$
$$HO—C_6H_4—OH \quad (26)$$

Now benzoquinone is reduced during all even-numbered waves, and the hydroquinone is oxidized (concomitantly with PAP) during the third, and all subsequent odd-numbered, transitions. The total transition times under these conditions follow the diffusion-controlled case, as noted also by Testa and Reinmuth (9), since any benzoquinone imine which hydrolyzes forms a species

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Table I. Relative Transition Times for Cyclic Chronopotentiometry with Following Chemical Reaction

For all cases, $i_{Red} = i_{Ox}$, and R initially absent

a_n

n	Diffusion-controlled case (5)	Case 1, kinetic reaction $k\tau_1 = 0.2$	$k\tau_1 = 0.5$	$k\tau_1 = 1.0$	$k\tau_1 = 1.5$	Case 2, catalytic reaction $k\tau_1 = 0.2$	$k\tau_1 = 0.5$	$k\tau_1 = 1.0$	$k\tau_1 = 1.5$	Case 3, kinetic-catalytic $k_1 = k_2 \quad \tau_1 = 1.0$ = 0.5
1	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
2	0.333	0.282	0.227	0.167	0.130	0.282	0.227	0.167	0.130	0.167
3	0.588	0.530	0.463	0.384	0.328	0.607	0.634	0.673	0.707	0.468
4	0.355	0.272	0.200	0.138	0.104	0.294	0.232	0.169	0.130	0.149
5	0.546	0.457	0.373	0.292	0.243	0.573	0.609	0.658	0.699	0.380
6	0.366	0.259	0.180	0.120	0.090	0.298	0.233	0.169	0.130	0.136
7	0.525	0.413	0.321	0.243	0.200	0.559	0.600	0.655	0.697	0.330
8	0.373	0.246	0.165	0.108	0.081	0.301	0.234	0.169	0.130	0.126
9	0.513	0.380	0.285	0.211	0.173	0.551	0.597	0.654	0.697	0.296
10	0.378	0.235	0.153	0.099	0.075	0.302	0.234	0.169	0.130	0.119
11	0.504	0.354	0.259	0.189	0.155	0.547	0.595	0.654	0.697	0.270
12	0.382	0.225	0.143	0.093	0.070	0.303	0.234	0.169	0.130	0.113
13	0.498	0.333	0.238	0.172	0.141	0.544	0.594	0.653	0.697	0.250
14	0.385	0.216	0.135	0.087	0.066	0.304	0.234	0.169	0.130	0.108
15	0.493	0.316	0.221	0.159	0.130	0.542	0.594	0.653	0.697	0.234
16	0.388	0.207	0.128	0.082	0.062	0.305	0.234	0.169	0.130	0.104
17	0.489	0.300	0.208	0.149	0.121	0.541	0.594	0.653	0.697	0.221
18	0.390	0.200	0.122	0.079	0.060	0.305	0.234	0.169	0.130	0.100
19	0.486	0.287	0.196	0.140	0.113	0.540	0.594	0.653	0.697	0.210
20	0.392	0.193	0.117	0.075	0.057	0.305	0.235	0.169	0.130	0.097

Table II. Relative Transition Times for Cyclic Chronopotentiometry of Titanium(IV) in Absence and Presence of Hydroxylamine

A. Solution contained 0.5mM titanium (IV) chloride and 0.2M $H_2C_2O_4$. The current density was 0.0567 ma. per sq. cm. at a mercury pool electrode. τ_1 was 5.0 sec., temperature 23° C.

| | a_n | |
| | | Theoretical (diffusion) |
n	Experimental	controlled
1	1.000	1.000
2	0.350	0.333
3	0.588	0.588
4	0.368	0.355
5	0.564	0.546
6	0.372	0.366
7	0.518	0.525
8	0.372	0.373
9	0.490	0.513
10	0.372	0.378

B. Solution contained 0.4mM titanium (IV) chloride, 0.2M $H_2C_2O_4$, and 0.01M hydroxylamine hydrochloride. The current density was 0.0678 ma. per sq. cm. at mercury pool electrode. τ_1 was 4.7 sec., temperature 23° C.

| | a_n | |
| | | Theoretical (catalytic reaction |
n	Experimental	$k\tau_1 = 1.1$)
1	1.000	1.000
2	0.159	0.158
3	0.522	0 680
4	0.163	0.159
5	0.460	0.667
6	0.163	0.160
7	0.460	0.664
8	0.163	0.160
9	0.460	0.663
10	0.165	0.160

which is electroactive under these conditions.

The search for systems which follow the catalytic scheme, Case 2, was less successful. Some systems, such as iron(III) reduction in the presence of H_2O_2, and titanium(IV) reduction in the presence of chlorate ion, were found to have a rate constant for the catalytic reaction which was too large to be studied conveniently with the present apparatus. The oxidation of iodide in the presence of oxalate ion involved a more satisfactory rate constant, but was complicated by the adsorption of iodine on the electrode. The reduction of titanium(IV) in the presence of hydroxylamine (which can oxidize titanous ion produced at the electrode) has been investigated using electrochemical techniques [see (1, 3) and references contained therein] and appeared to have a suitable rate constant. CC of titanium(IV) alone indicated that the system followed the simple diffusion-controlled reaction model (Table II). Upon addition of hydroxylamine, the first transition time was

Program in Fortran 60

```
C     CYCLIC CHRONO KINETIC AND CATALYTIC CASE COMBINED PLANE ELECTODE
C     READ IN K, NOSIG, RR, RK1, RK2, T(1)
      DIMENSION X(100),T(100),R(100)
      READ 900, K, NOSIG, RR, RK1, RK2, T(1)
63    V = 2. * SQRTF (T(1)/3.14159 ) * RK2 / (RK1+ RK2) + ( 1. / SQRTF (RK1 + RK2 ))
      * ERFUN ( SQRTF ((RK1 + RK2) * T(1))) *RK1/(RK1 + RK2)
      CENERATION OF EQUATIONS
      DO 200 N = 2, K
      T(N) = 0.0
      M = 1
      LA = O
10    DO 80 I=1,N
      SUM = 0.0
      DO 60 J=I,N
60    SUM = SUM + T(J)
      IF ( XMODF( N,2)) 62, 61, 62
62    X (I ) = 2. * SQRTF ( SUM / 3.14159) * RK2 / (RK1 + RK2) + (1. / SQRTF
      (RK1 + RK2 )) * ERFUN ( SQRTF ((RK1 + RK2) * SUM)) * RK1 / ( RK1 + RK2)
      GO TO 80
61    X(I) = ERFUN(SQRTF((RK1 + RK2)*SUM))
80    CONTINUE
      Y = X(1) — V
81    SIGN = 1.0
      DO 95 L = 2,N
      SIGN = —SIGN
95    Y = Y + SIGN * RR * X(L) — SIGN*V
C  2  SOLVE GENERATED EQUATION BEGIN AT 96 READ IN NOSIG FOR ACCURACY
96    IF(M—1)300,100,102
100   Z = Y
      M = M + 1
102   IF (Z) 98,200,99
98    IF (Y) 71,200,73
99    IF (Y) 73, 200, 71
71    T(N) = T(N) + 10.0 **(—LA)
      GO TO 10
73    T(N) = T(N) — 10.0 **(—LA)
      LA = LA + 1
199   IF ((T(N)/10.0**(—LA)) — 10.0 **(NOSIG)) 71, 200, 200
200   CONTINUE
C  3  EQUATION SOLVED PRINT ANSWER
      DO 201 J=1,K
201   R(J) = T(J)/T(1)
      PRINT 903, RR, T(1) , RK1 , RK2
      PRINT 901
      PRINT 902,(N,T(N),R(N),N=1,K)
500   CONTINUE
900   FORMAT (2I10, 4F10.5)
901   FORMAT (4(3X, 1HN, 6X, 4H TAU, 5X, 5HRATIO)//)
902   FORMAT (4(1X, 1I3, 2F10.6)/)
903   FORMAT ( 2X, 5HRR = , 1X, F10.5, 1X, 7HT(1) = , 1X, F10.5, 1X, 6HRK1 =
      , F10.5, 1X, 6HRK2 = , F10.5)
904   FORMAT ( 110)
      GO TO 920
300   PRINT 905
905   FORMAT (2X, 5HERROR)
920   STOP
      END
      FUNCTION ERFUN (X)
      IF (X) 8,8,5
8     ERFUN = 0.0
      RETURN
5     IF ( X— 3.1) 7, 7, 4
7     T = X * 2.0/ 1.7724538509
      ERFUN = T
      TERM = 2.0
2     T = —T* X* X* (TERM — 1.0)/((TERM + 1.0)* (TERM / 2.0))
      TERM = TERM + 2.0
      ERFUN = ERFUN + T
      IF ( X — 1.0 ) 3,10, 10
3     TERFUN = ERFUN
      GO TO 12
10    TERFUN = 1.0 — ERFUN
12    TEST = ABSF ( T/ TERFUN)
      IF ( TEST — 1.E—6) 1,1,2
1     ERFUN = ERFUN
      RETURN
4     T = 1.0/(1.7724538509 * X) * EXPF (—X*X)
      EXERFC = T
      TERM = 1.0
11    T = —T* TERM /(2.0*X*X)
      TERM = TERM + 2.0
      EXERFC = EXERFC + T
      TEST = ABSF (T/EXERFC)
      IF ( TEST — 1.E — 4) 9,9,11
9     ERFUN = 1.0 — EXERFC
      RETURN
      END
      END
```

enhanced, and the second decreased, as expected for a catalytic system. However, the third and subsequent relative transition times did not follow the theoretical model (Table II). The third transition time was much lower than that predicted for a reaction with a rate constant fitting the first two transition times, and was in fact even lower than the value expected for a simple diffusion-controlled case. This finding prompted the solution of Case 3, involving both catalytic and kinetic irreversible reactions. However a good agreement between theory and experiment could not be obtained for this case either; the predicted slow decrease in the relative transition times was not observed experimentally. The reaction system involving titanium(IV) and hydroxylamine is apparently more complicated than has been suspected, and is being investigated further.

CC has the advantage of allowing the determination of rate constants for an experiment at a single current density. Furthermore differentiation between kinetic and catalytic cases is immediately apparent in a single experiment, as opposed to chronopotentiometry with a single current reversal. Complications due to additional reactions, such as the case of titanium(IV) and hydroxylamine, or due to adsorption are readily recognized.

APPENDIX

Computer Program for Generating and Solving Equations for CC with Following Chemical Reaction. This program in Fortran 60 generates and solves the equations for the various relative transition times. The following data are read in: K, the total number of reversals desired, NOSIG, the number of significant figures desired in a_n, $(i_{Red} + i_{ox})/i_{Red}$ (RR), k_1 (RK 1), the rate constant for the catalytic reaction, k_2 (RK 2), the rate constant for the kinetic reaction, and τ_1 [T(1)], the first transition time. The output involves printing the above data and also $k\tau_n$ [T (N)] and a_n [R (N)]. This program can be used for all three cases. For Case 1, set RK 1 = 0.0 and T (1) = 1.0. For Case 2, set RK 2 = 0.0 and T (1) = 1.0. For Case 3, set RK 1, RK 2, and T (1) at desired values. To form tables of a_n's for different values of k_1 and k_2, a DO-loop can be added, starting with the statement before READ 900 and ending on the 500 CONTINUE statement.

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Electrode Reactions of Aromatic Compounds in Strong Acid Solutions

Chronopotentiometric and Spectrometric Studies of the p-Hydroquinone–H₂SO₄ System at Platinum Electrodes

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▶ The electro-oxidation of p-hydroquinone and the subsequent reduction of the electro-oxidation products at platinum electrodes has been studied chronopotentiometrically in supporting electrolytes of varying sulfuric acid concentration. Five distinct anodic waves are found between 10 and 16F H₂SO₄ which represent the oxidation of hydroquinone and four new species formed at high acid strengths. Reverse current chronopotentiograms reveal that only two oxidation products are observed in this acid strength range even though the total reverse transition time was in all cases equal to ¹/₃ the anodic electrolysis time. Ultraviolet and nuclear magnetic resonance spectra as well as electrochemical evidence indicate that the four new species are sulfonation products rather than protonation compounds. The four compounds and their oxidation products are identified.

THE ELECTRODE reactions of aromatic compounds such as the phenylenediamine isomers and related diamines (*23*, *29*, *34*, *36*), p-aminophenol (*43*, *45*), N,N-dimethylaniline (*9*, *11*, *31*), chloropromazine (*36*), and nitrobenzene compounds (*12*, *28*, *36*) have been the subject of considerable interest in recent years. Quite often the electrode mechanisms of this type of compound involve the formation of short-lived intermediates such as both negative and positive free radicals (*28*, *36*), carbonium ions (*9*, *11*, *31*) and imines (*9*, *11*, *31*, *45*). The nature and reactions of some of these intermediates can be studied by means of such electrochemical techniques as reverse current chronopotentiometry (*7*, *38*, *45*, *46*), rotating disk electrodes (*10*, *11*, *24*), and cyclic voltametry (*11*, *19*, *31*, *39*). These techniques are generally employed in conjunction with electron paramagnetic resonance (EPR) (*12*, *28*,

36) and spectrophotometric (*31*) studies. Such investigations have not only elucidated the electrode behavior of many organic compounds but have also shed considerable light on the chemistry of these short-lived intermediates. This information is very useful also to the organic chemist as it results in a better understanding of homogeneous organic reaction mechanisms in general.

A recent study of the anodic oxidation of phenylenediamine compounds (*29*) as a function acid strength of the supporting electrolyte showed that total protonation of the basic amine groups had a very large effect on the oxidation potential. Protonation of just one amino group (one free amino group remains) had no observable effect on the

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