Chronopotentiometric Measurements of Chemical Reaction Rates. I. Programmed Current Studies of the ECE Mechanism[1]

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Programmed current chronopotentiometry, specifically current reversal and current decrease, is applied to electrode reactions characterized by a chemical reaction coupled between two charge-transfer reactions, the ECE mechanism. The equations for the transition times are derived and solved. Current-reversal results on systems following the ECE mechanism, *p*-nitrosophenol, *p*-nitrophenol, and *o*-nitrophenol, are in good agreement with those obtained by single transition time chronopotentiometry and potentiostatic investigations. A mechanism is suggested for these electrode and chemical reactions.

Introduction

Chronopotentiometry has been recognized as a potentially important tool in the measurement of rate constants of chemical reactions concurrent with the electrode process.[2] The boundary value problem in chronopotentiometry, unlike that in polarography, can usually be solved explicitly, since the flux at the electrode surface is known. The variation of the chronopotentiometric transition time constant ($i\tau^{1/2}/C$), based only on the first transition time, has been used to calculate the rate constants of chemical reactions, for example, when the starting material is regenerated[3,4] (a catalytic reaction) or when a chemical reaction is interposed between two charge-transfer reactions[5,6] (the ECE mechanism). Programmed current techniques have the advantage of allowing calculation of the rate constant without knowing the transition time in the absence of the perturbing chemical reaction or even the concentration, diffusion coefficient, and current density. Many times the latter two variables can only be estimated, severely limiting the accuracy of the calculated rate constant. The value of current-reversal techniques has been demonstrated by current-reversal chronopotentiometry and cyclic chronopotentiometry in the measurement of the rate constants of the hydrolysis of electrochemically generated *p*-quinoneimine[7,8] and the reaction of electrochemically generated Ti(III) with hydroxylamine.[3,8,9]

The present study was undertaken with the aim of applying current decrease and current-reversal methods to compounds following the ECE mechanism. The ECE scheme can be represented by

$$A + n_1e \longrightarrow B \xrightarrow{k} C + n_2e \longrightarrow D \qquad (1)$$

and on current reversal

$$B - n_3e \longrightarrow E \qquad C + n_2e \longrightarrow D \qquad (2)$$

The ECE mechanism under consideration in this study is the one in which C is reduced at potentials considerably less cathodic than those required to reduce A, so that upon current reversal, at potentials where B is being oxidized, C continues to reduce. Previous results on the polarographic reduction of *p*- and *o*-nitrophenol and *p*-nitrosophenol were explained by the above scheme.[2,10] The polarographic diffusion current constant corresponded approximately to a six-electron process (four in the case of the *p*-nitroso compound) at both high and low pH. Intermediate pH measure-

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[1] This work supported by the Robert A. Welch Foundation and the National Science Foundation (GP-1921).

[2] P. Delahay, *Discussions Faraday Soc.*, **17**, 205 (1954).

[3] C. Furlani and G. Morpugo, *J. Electroanal. Chem.*, **1**, 351 (1960).

[4] P. Delahay, C. Mattox, and T. Berzins, *J. Am. Chem. Soc.*, **76**, 5319 (1954).

[5] A. C. Testa and W. H. Reinmuth, *ibid.*, **83**, 784 (1961).

[6] G. S. Alberts and I. Shain, *Anal. Chem.*, **35**, 1859 (1963).

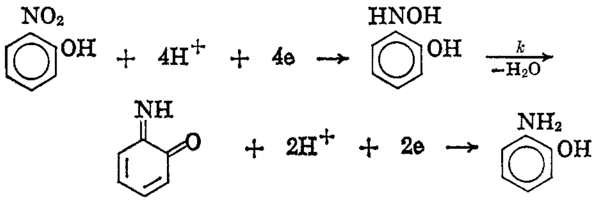
[7] A. C. Testa and W. H. Reinmuth, *ibid.*, **32**, 1512 (1960).

[8] H. B. Herman and A. J. Bard, *ibid.*, **36**, 510 (1964).

[9] J. H. Christe and G. Lauer, *ibid.*, **36**, 2037 (1964).

[10] D. Stočesová, *Collection Czech. Chem. Commun.*, **14**, 615 (1949).

ments revealed that this constant passed through a minimum. While no rate constant was actually calculated—the boundary value problem is quite difficult—the data were interpreted by Stočesová[10] for the system *o*-nitrophenol, to be an acid–base catalyzed decomposition of the product of the first electrode reaction, *o*-hydroxylaminophenol. The product of the chemical reaction, *o*-quinoneimine, was assumed to be further reduced at these potentials giving, if the chemical reaction is fast, an over-all six-electron reduction. The reaction mechanism proposed was



(3)

The above mechanism was used by Testa and Reinmuth[5] in their chronopotentiometric measurements on *o*-nitrophenol and Alberts and Shain[6] in their measurements on *p*-nitrosophenol. Both authors found comparatively large errors in the ordinary chronopotentiometric determination of the rate constant principally because the data had to be fitted to a two-parameter plot. It appeared likely that a current-reversal technique could circumvent some of these difficulties and allow a more precise measurement of the rate constant of this fairly general chemical reaction.

Theory

Current Decrease. The Murray–Reilley[11] current response function has proven quite valuable in the solution of the partial differential equations for chronopotentiometry with programmed current. The availability of solutions for many schemes with kinetic complications[12] allows one to obtain a result for current decrease by using the current response function in a rather straightforward manner. Thus if the concentration at the electrode surface, $C(0, t)$, before the first transition time can be represented by

$$C^0 - C(0, t) = \mathrm{f}(t) \tag{4}$$

where C^0 is the original concentration of the electroactive material, the transition time for a current decrease, when the surface concentration of the original material again falls to zero, is obtained by solving

$$\mathrm{f}(\tau_1) = \mathrm{f}(\tau_1 + \tau_2) - R\mathrm{f}(\tau_2) \tag{5}$$

and

$$R = (i_2 - i_1)/i_1 \tag{6}$$

where τ_1 and τ_2 are the first and second transition times and i_1 and i_2 are the applied currents before and after current decrease.

Testa and Reinmuth[13] have given $\mathrm{f}(t)$ in (4) for the ECE mechanism. The partial differential equations that apply to the ECE scheme are given in the Appendix. Rearranging the solution [eq 21 in ref 14] (see also Appendix) yields

$$\mathrm{f}(t) = (i\rho/n_2FD^{1/2})\Big[2t^{1/2}/\pi^{1/2} + (\rho/k^{1/2})\ \mathrm{erf}[(kt)^{1/2}] + \frac{a^{1/2}\rho^2 \exp(-at)}{k\pi^{1/2}}\{\Phi[\rho(at)^{1/2}] + \Phi[(at)^{1/2}]\}\Big] \tag{7}$$

where $\Phi(x) = \int_0^x \exp(\mu^2)\mathrm{d}\mu$, $a = k/(1 - \rho^2)$, $\rho = n_2/(n_2 + n_1)$, k is the pseudo-first-order rate constant, and the other symbols have their usual meaning.

Equation 4 was solved using (7) as $\mathrm{f}(t)$ on a digital computer. The program was similar to the one used to solve for the amount adsorbed on an electrode using current reversal.[14] Solution for the root of any nonlinear equation is possible under the following conditions: the equation has only one positive root and a number less than the root is known. In this case the solution was double valued and the program was modified to solve for both roots. The results are given in Table I. The ratio τ_2/τ_1 in absence of a chemical reaction ($k = 0$) was calculated using a rearranged form of the equation (11)[13] derived by Testa and Reinmuth.

$$\tau_2/\tau_1 = 4R^2/(R^2 - 1)^2 \tag{8}$$

In both cases, $\rho = {}^1/_2$ and ${}^1/_3$, the ratio goes through a maximum. The system is therefore diffusion controlled at both large and small values of $k\tau$; in order to observe the kinetic effect it is necessary to pick an intermediate transition time. Since the solution is double valued, a rate constant cannot be calculated from one measurement; two are needed. Even systems which are completely irreversible, *i.e.*, B is not oxidizable, can be studied by current-decrease techniques. However, a forward transition must be observed, which may prove a disadvantage in systems yielding ill-defined transitions.

Current Reversal. The transition time for current reversal, when the concentration of the electrode

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(11) R. W. Murray and C. N. Reilley, *J. Electroanal. Chem.*, **3**, 182 (1962).

(12) C. N. Reilley in "Treatise on Analytical Chemistry," Part I, Vol. IV, I. M. Kolthoff and P. J. Elving, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 2151.

(13) A. C. Testa and W. H. Reinmuth, *Anal. Chem.*, **33**, 1320 (1961).

(14) H. B. Herman, S. V. Tatwawadi, and A. J. Bard, *ibid.*, **35**, 2210 (1963).

Table I: Relative Transition Times for ECE Current Decrease

	τ_2/τ_1			
	R			
$k\tau_1$	0.20	0.30	0.40	0.50
		$\rho = 1/2$		
0.0	0.174	0.435	0.907	1.778
0.2	0.264	0.710	1.668	3.928
0.4	0.362	1.052	2.490	5.302
0.6	0.487	1.309	2.807	5.417
0.8	0.569	1.412	2.811	5.211
1.0	0.611	1.420	2.711	4.940
1.2	0.624	1.383	2.582	4.675
1.4	0.619	1.329	2.455	4.434
1.6	0.604	1.272	2.338	4.222
1.8	0.585	1.218	2.233	4.039
2.0	0.565	1.168	2.141	3.880
		$\rho = 1/3$		
0.0	0.174	0.435	0.907	1.778
0.2	0.213	0.549	1.201	2.534
0.4	0.251	0.658	1.462	3.075
0.6	0.286	0.746	1.629	3.295
0.8	0.313	0.806	1.706	3.334
1.0	0.334	0.839	1.728	3.298
1.2	0.348	0.853	1.718	3.235
1.4	0.356	0.855	1.693	3.162
1.6	0.360	0.849	1.661	3.089
1.8	0.360	0.838	1.627	3.021
2.0	0.359	0.826	1.594	2.957

product falls to zero, was obtained using the step-function theorem.[15] Since in the ECE scheme, the flux of B is not constant, the current due to the electrolysis of B must be calculated. The procedure involves defining a new variable whose solution and flux are known, in order to solve for the unknown flux of B. The method is detailed in the Appendix and closely follows the one described by Testa and Reinmuth[13] and King and Reilley.[16] The result of this calculation yields the surface concentration of B on current reversal

$$C_B(0, t) = g(t, \rho) + (1 - R)g(t - \tau_1, \rho') - g(t - \tau_1, \rho) \quad (9)$$

where

$$g(t, \rho) = (i\rho/n_2FD^{1/2})[k^{-1/2} \operatorname{erf}[(kt)^{1/2}] + (2\rho a^{1/2}/k\pi^{1/2}) \exp(-at)\{\Phi[(at)^{1/2}] + \Phi[(a - k)^{1/2}t^{1/2}]\}] \quad (10)$$

$\rho = n_2/(n_1 + n_2)$, $\rho' = n_2/(n_2 + n_3)$, $a = k/(1 - \rho^2)$, and $g(t - \tau_1, \rho')$ denotes the same expression as (10) with all t's replaced by $(t - \tau_1)$ and all ρ's replaced by ρ'. When $\rho = \rho'$, as in the case of nitrosophenols, (9) simplifies to

$$C_B(0, t) = g(t, \rho) - Rg(t - \tau_1, \rho) \quad (11)$$

When $\rho \neq \rho'$, as in the case of nitrophenols, (10) is approximate (see Appendix). When (10) is multiplied by $\tau_1^{-1/2}$, the equation is in terms of the dimensionless quantity $k\tau_1$. At $t = \tau_1 + \tau_2$, $C_B(0, t) = 0$, and solution of (9) under these conditions yields values of τ_2/τ_1 as a function of $k\tau_1$. The results of such calculations, using the previously mentioned computer program, are given in Table II.

Table II: Relative Transition Times for ECE Current Reversal

$k\tau_1$	$\rho = 1/2$ $\rho' = 1/2$ $R = 2.0$ τ_2/τ_1	$\rho = 1/2$ $\rho' = 1/3$ $R = 2.0$ τ_2/τ_1	$\rho = 1/2$ $\rho' = 1/3$ $R = 1.5$ τ_2/τ_1	$\rho = 1/3$ $\rho' = 1/3$ $R = 2.0$ τ_2/τ_1
0.00	0.333	0.125	0.333	0.333
0.10	0.281	0.112	0.294	0.293
0.20	0.241	0.101	0.263	0.260
0.30	0.208	0.092	0.236	0.233
0.40	0.182	0.084	0.213	0.210
0.50	0.160	0.076	0.193	0.190
0.60	0.142	0.069	0.175	0.172
0.70	0.127	0.064	0.160	0.157
0.80	0.114	0.059	0.148	0.144
0.90	0.102	0.055	0.136	0.133
1.00	0.093	0.051	0.126	0.123
1.20	0.077	0.044	0.108	0.106
1.40	0.065	0.039	0.095	0.092
1.60	0.056	0.034	0.084	0.081
1.80	0.049	0.030	0.074	0.072
2.00	0.043	0.027	0.066	0.065

In some cases it is necessary to decrease the current on reversal because with equal current densities the transition time ratio may be too small to be measured conveniently.

In the current-reversal technique it is not necessary to reach the first transition time; the current can be reversed at any point along the wave and a rate constant can be calculated. If the first transition time is not well defined, this offers a decided advantage. The solutions are single valued and it appears that the method is experimentally more precise than the current-decrease method.

Results and Discussion

Forward Transition Time Studies. Alberts and Shain,[6] in a comparison of potentiostatic and chronopotentiometric methods, found that the rate constant

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(15) R. V. Churchill, "Operational Mathematics," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1958, p 23.

(16) R. M. King and C. N. Reilley, *J. Electroanal. Chem.*, **1**, 434 (1960).

calculated from the first transition time in the reduction of *p*-nitrosophenol exhibited a disturbing trend; at high current densities the calculated rate constant increased. Three sources of error were postulated: (1) the assumption that the concentration product of the chemical reaction, C, was zero at the electrode surface was false; (2) material A was adsorbed on the electrode surface; (3) and/or an appreciable fraction of the current was needed to charge the double layer. These postulates will be examined below.

The chronopotentiometric measurements on *p*-nitrosophenol were repeated under slightly different conditions and the results of Alberts and Shain were confirmed. Table III shows the results on that system and on *p*-nitrophenol. The observed increase in the calculated rate constant becomes apparent at slightly shorter transition times, since the concentration was about three times higher than that used by Alberts and Shain. This suggests that postulates 2 and 3 are more likely. Postulate 1 can be eliminated by examination of the potential–time curves of *p*-nitrosophenol using cyclic chronopotentiometry. A reversible couple corresponding to *p*-nitrosophenol (A) and *p*-hydroxylaminophenol (B) is set up around -0.1 v *vs.* sce. When wider potential limits are set, another couple is observed very close to the mercury oxidation wave, at least 0.3 v more anodic than the first couple. This corresponds to the reduction of *p*-quinoneimine (C) and the oxidation of *p*-aminophenol (D) and indicates that the concentration of C would indeed be zero at the electrode surface at potentials where A is reduced and B is oxidized.[17]

Table III: Chronopotentiometric Calculation of the Rate Constant of the Product of the Reduction of *p*-Nitrosophenol and *p*-Nitrophenol[a]

$i\tau^{1/2}_{\infty}/i\tau^{1/2}$	τ, sec	k, sec^{-1}	$i\tau^{1/2}_{\infty}/i\tau^{1/2}$	τ, sec	k, sec^{-1}
A. 3.0 m*M* *p*-nitrosophenol			B. 2.1 m*M* *p*-nitrophenol		
1.09	42.6	0.63	1.07	37.4	0.52
1.14	20.2	0.58	1.09	18.35	0.66
1.21	9.34	0.61	1.14	8.73	0.61
1.31	4.03	0.73	1.24	3.75	0.53
1.57	1.24	0.81	1.29	0.788	1.70
1.63	0.59	1.35	1.32	0.373	2.81

[a] Conditions: 0.1 *M* acetic acid, 0.1 *M* potassium acetate, 0.2 *M* potassium nitrate, and 20% ethanol (v/v) and at a mercury pool electrode (3.2 cm^2), temperature 24.2°.

Since the nitro group is reduced in a four-electron step to hydroxylamine, the product of the reduction of *p*-nitrophenol is identical with the product of the *p*-nitroso compound. If we are measuring the chemical rate constant of the dehydration of *p*-hydroxylaminophenol, the two compounds should yield the same rate constant. The agreement of the calculated rate constants in Table III suggests that the same intermediate is indeed produced in the two electrode reactions.

To determine if *p*-nitrosophenol is adsorbed on mercury, electrocapillary curves were recorded using drop-time measurements. Addition of *p*-nitrosophenol to the supporting electrolyte caused the drop time to be lowered, indicating adsorption. The amount adsorbed can be calculated from the relationship[18]

$$-\Gamma = \partial\sigma/RT\ \partial \ln C \qquad (12)$$

and

$$\Delta\sigma = 38.0\Delta t \qquad (13)$$

where Γ is the surface excess, σ is the surface tension, and Δt is the amount the drop time has been lowered. The value calculated for Γ was $(0.13 \pm 0.07) \times 10^{-9}$ mole/cm^2. The large deviation results from the small change in drop time (a few hundreths of a second) on increasing concentration. Recently, the chronopotentiometric data of Alberts and Shain[6] were reinterpreted by Evans[19] to account for the increase in the calculated rate constant of *p*-nitrosophenol at short times. He applied an empirical correction factor to the current until the calculated rate constant agreed with the potentiostatic results. The correction factor in millicoulombs corresponded approximately to the estimated amount of charge needed to charge the mercury double layer. However, the voltage range assumed by Evans, 1 v, was probably too large for this system, since the quarter-wave potential is only about -0.1 v *vs.* sce. In addition, the double-layer capacity is probably further reduced in the presence of adsorption.[18] The amount of adsorption found in this study, even with the large relative deviation, almost exactly accounts for the observed increase in the rate constant. If the adsorbed species is electrolyzed simultaneously with the diffusing species (mechanism 3 in ref 20), the observed transition time will be longer. This effect is more important at short times. If we assume that Γ is the same in both studies, even though the conditions are slightly different, a correction factor of 1.8 μcoulombs is calculated. Evans[19] found em-

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(17) Similar results were obtained by R. S. Nicholson and I. Shain, *Anal. Chem.*, **37**, 190 (1965), using stationary electrode polarography.

(18) P. Corbusier and L. Gierst, *Anal. Chim. Acta*, **15**, 254 (1956).

(19) D. H. Evans, *Anal. Chem.*, **36**, 2027 (1964).

(20) S. V. Tatwawadi and A. J. Bard, *ibid.*, **36**, 2 (1964).

pirically that 1.7 μcoulombs gave the best fit to the data.

Programmed Current Studies. Current-decrease chronopotentiometry was performed on *p*-nitrophenol and *o*-nitrophenol at relatively long times (7–10 sec) under the same conditions as in Table III. The second transition time was very poorly defined and good measurements could not be made. The uncertainty in the data made it very difficult to pick the correct value of the rate constant from the double-valued function. The current-decrease results would probably have been better at higher current densities, but current-reversal techniques, described below, were more convenient.

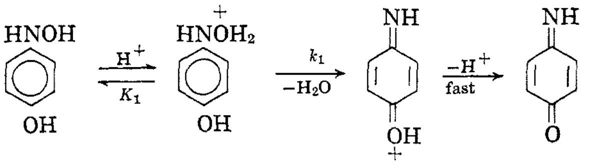
Current-reversal chronopotentiometry was performed on *p*-nitrosophenol, *p*-nitrophenol, and *o*-nitrophenol. The results are shown in Table IV. Again *p*-nitrosophenol and *p*-nitrophenol yielded the same rate constant as expected. The data for these two systems agree well with the results of single transition time chronopotentiometry and chronoamperometry[6] with no discernible trend. *o*-Nitrophenol does show a small trend in the calculated rate constant and it may be that, because of the longer times needed to perform the measurement, spherical corrections become more important.

Table IV: Current-Reversal Calculation of the Rate Constant (Conditions Same as in Table III except at Hanging Mercury Drop (Area 0.036 cm², Temperature 24.8°)

τ_1, sec	τ_2/τ_1	$k\tau_1$	k, sec^{-1}
A. 2.0 m*M* *p*-nitrosophenol, $R = 2.0$			
0.35	0.270	0.13	0.38
0.49	0.216	0.28	0.57
0.68	0.176	0.42	0.62
0.83	0.160	0.50	0.60
1.15	0.143	0.60	0.52
2.40	0.080	1.16	0.48
		Av	0.56 ± 0.04
B. 1.8 m*M* *p*-nitrophenol, $R = 1.5$			
0.162	0.320	...	...
0.690	0.220	0.37	0.54
0.870	0.190	0.52	0.60
0.930	0.178	0.58	0.62
3.160	0.078	1.72	0.54
4.200	0.071	1.89	0.45
		Av	0.55 ± 0.07
C. 1.4 m*M* *o*-nitrophenol, $R = 1.5$			
1.43	0.250	0.25	0.18
1.91	0.214	0.40	0.21
2.82	0.187	0.53	0.19
3.33	0.176	0.59	0.18
4.00	0.188	0.53	0.13
4.29	0.166	0.66	0.15
7.38	0.152	0.76	0.11
8.40	0.143	0.83	0.10
8.83	0.170	0.64	0.07
10.53	0.121	1.05	0.10
		Av	0.14 ± 0.05

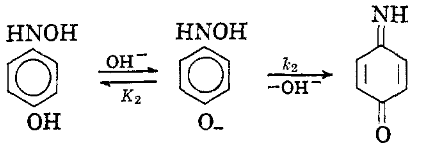
Testa and Reinmuth[5] determined the mechanism of the reduction of *o*-nitrophenol by chronopotentiometry. In that study they indirectly disproved an alternate hypothesis of a preceeding chemical reaction. Current-reversal chronopotentiometry immediately differentiates between the two mechanisms. If a preceding chemical reaction were occurring, the transition time ratio, τ_2/τ_1, would correspond to diffusion control, since the product is not involved in chemical reaction. For the ECE mechanism, τ_2/τ_1 would vary as described in Table II.

Mechanism. From the pH dependence of the polarographic limiting current, Stočesová[10] suggested that the chemical reaction of *o*-hydroxylphenylhydroxylamine was acid-base catalyzed. A mechanism has already been proposed[21] to explain the acid-base catalyzed rearrangement of phenylhydroxylamine. This mechanism can be adapted to the catalysis of the product of the reduction of nitrophenols and nitrosophenols. Thus for the *p*-compounds at low pH



(14)

and at high pH



(15)

If the first-order rate constant is proportional to the concentration of hydrogen ion in the first equilibrium, as is the case in the rearrangement of phenylhydroxylamine,[21] the acid–base dependence on the rate can be calculated. Thus at low pH

$$dC_B/dt = k_1K_1[H^+][B] \qquad (16)$$

k_1 is the first-order rate constant for the acid-catalyzed

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[21] H. E. Heller, E. D. Hughes, and C. K. Ingold, *Nature*, **168**, 909 (1951).

reaction and K_1 is the equilibrium constant for the first equilibrium in (14). At high pH

$$dC_B/dt = k_2K_2[OH^-][BOH] \qquad (17)$$

where k_2 is the first-order rate constant for the base-catalyzed reaction and K_2 is the equilibrium constant for the first equilibrium in (15). In both cases, B and BOH are *p*-hydroxylphenylhydroxylamine. Further studies are being made on the dependence of the rate constant on pH to see if the proposed mechanism is followed.

Experimental Section

The behavior of the first transition time of *p*-nitrosophenol and *p*-nitrophenol at a mercury pool electrode was investigated using the apparatus previously described.[8] The transition times were measured by starting the digital counter at the instant of applying current and stopping it with a triggered relay at the potential break. Current-decrease measurements were made by modifying the above circuit so that the relay inserted a large resistor in series with the power supply after the first potential break.

The variation of the transition time ratio with the time of current reversal at a hanging mercury drop (area 0.038 cm^2) was investigated with an operational amplifier constant current source and potential-sensitive switch.[22] The potential–time curves were recorded as before[23] except that the oscilloscope trace was modulated by applying square waves from a low-frequency function generator (Hewlett-Packard Model 202A) in its *Z* input. The transition-time ratios were measured by counting the dots appearing in the trace and multiplying by the reciprocal of the frequency of the generator.

The sodium salt of *p*-nitrosophenol (Eastman Kodak Co.) was purified according to the procedure given by Alberts and Shain.[6] *p*-Nitrophenol and *m*-nitrophenol (both from Eastman Kodak Co.) were recrystallyzed from benzene, and *o*-nitrophenol (Eastman Kodak Co.) from water–ethanol mixtures. The *p*-nitrosophenol was weighed into a deaerated solution before measurement. The acetic acid used as supporting electrolyte was standardized by titration with commercially standardized sodium hydroxide. Potassium acetate and potassium nitrate were weighed out directly. The pH of the supporting electrolyte was 4.92.

Electrocapillary curves were determined by the drop-time technique of Corbusier and Gierst[18] using the previously described apparatus.[24]

Acknowledgment. The authors are grateful for helpful discussions with Nathan Bauld about the mechanism and to John Bowman for making some of the experimental measurements.

Appendix

Mathematical Solution of ECE Mechanism Equations for Chronopotentiometry

The mathematical solution of Fick's second-law equations and the appropriate boundary conditions follow essentially the treatment of Testa and Reinmuth.[13] In order to solve explicitly for the reverse transition time and to indicate approximations in the case where the intermediate product is not oxidized back to the starting material ($\rho \neq \rho'$) a complete derivation of the equations is given.

Forward Transition Time. The ECE mechanism, eq 1, is described by the equations

$$(\partial C_A/\partial t) = D(\partial^2 C_A/\partial x^2) \qquad (1a)$$

$$(\partial C_B/\partial t) = D(\partial^2 C_B/\partial x^2) - kC_B \qquad (2a)$$

$$(\partial C_C/\partial t) = D(\partial^2 C_C/\partial x^2) + kC_B \qquad (3a)$$

$$t = 0, x \longrightarrow \infty; \quad C_A = C^0{}_A, C_B = C_C = 0 \qquad (4a)$$

$$x = 0; \quad C_C = 0 \qquad (5a)$$

For $t < \tau_1$

$$(\partial C_B/\partial x)_{x=0} = -(\partial C_A/\partial x)_{x=0} \qquad (6a)$$

$$n_1(\partial C_A/\partial x)_{x=0} + n_2(\partial C_C/\partial x)_{x=0} = i/FD \qquad (7a)$$

The above equations assume that semiinfinite linear diffusion is the sole mode of mass transfer, that the diffusion coefficients of A, B, and C are equal, and that species C is reduced at potentials somewhat less cathodic than those for A, so that (5a) holds at all times. Let $i_j(t)$ represent the instantaneous current involved in the production or consumption of the *j*th species at time *t*, so that (7a) becomes

$$i_A(t) + i_C(t) = i \qquad (8a)$$

and (6a) yields

$$i_A(t)/n_1FD = (\partial C_A/\partial x)_{x=0} = -(\partial C_B/\partial x)_{x=0} \qquad (9a)$$

Let

$$\phi = C_B + C_C \qquad (10a)$$

Combination of (2a), (3a), and (10a) yields

$$(\partial\phi/\partial t) = D(\partial^2\phi/\partial x^2) \qquad (11a)$$

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(22) H. B. Herman and A. J. Bard, *Anal. Chem.*, **37**, 590 (1965).

(23) A. J. Bard, *ibid.*, **33**, 11 (1961).

(24) A. J. Bard and H. B. Herman, *ibid.*, **37**, 317 (1965).

Differentiation of (10a) with respect to x, at $x = 0$, and combination with (8a) and (9a) yield

$$(\partial\phi/\partial x)_{x=0} = \frac{i}{n_2FD} - \frac{i_A(t)}{n_2FD}\left(\frac{n_1 + n_2}{n_1}\right) \quad (12a)$$

Combination of (10a) and (4a) shows that

$$\phi(x, 0) = 0 \text{ and } \lim_{x\to\infty} \phi(x, t) = 0 \quad (13a)$$

Solving (11a), using (12a) and (13a) as boundary conditions gives, in the Laplace transform plane

$$n_2FD^{1/2}[\bar{C}_B(0, s) + \bar{C}_C(0, s)] = -s^{-1/2}\left[i/s - \bar{\imath}_A(s)\left(\frac{n_1 + n_2}{n_1}\right)\right] \quad (14a)$$

where $\bar{C}_B(0, s)$, $\bar{C}_C(0, s)$, and $\bar{\imath}_A(s)$ represent the Laplace transforms of $C_B(0, t)$, $C_C(0, t)$, and $i_A(t)$, respectively.

Direct solution of (2a), with boundary conditions (4a) and (9a) yields

$$n_1FD^{1/2}\bar{C}_B(0, s) = \bar{\imath}_A/(s + k)^{1/2} \quad (15a)$$

Combination of (14a), (15a), and (5a), yields, with some rearrangement

$$\bar{\imath}_A = \frac{n_1 i\rho}{n_2 s^{3/2}}\left[\frac{s^{1/2}(s + k)^{1/2}}{(s + k)^{1/2} - \rho s^{1/2}}\right] \quad (16a)$$

where $\rho = n_2/(n_1 + n_2)$. Combination of (15a) and (16a) gives an equation for $\bar{C}_B(0, s)$

$$FD^{1/2}\bar{C}_B(0, s) = \frac{i\rho}{n_2 s^{3/2}}\left[\frac{s^{1/2}}{(s + k)^{1/2} - \rho s^{1/2}}\right] \quad (17a)$$

Solution of (1a), using (4a) and (9a) as boundary conditions, and combination with (16a) yield the following expression for $\bar{C}_A(0, s)$[13]

$$FD^{1/2}\left[\frac{C^0{}_A}{s} - \bar{C}_A(0, s)\right] = \frac{i\rho}{n_2 s^{3/2}}\left[\frac{(s + k)^{1/2}}{(s + k)^{1/2} - \rho s^{1/2}}\right] \quad (18a)$$

Inverse transformation of (18a) yields eq 7 in the text.

Current Reversal, $n_1 = n_3$. To calculate the reverse transition time, τ_2, an expression for $\bar{C}_B$ must be obtained which holds at all times, and then an equation of the form

$$\bar{C}_B(0, s) = \bar{\imath}(s)\bar{S}(s) \quad (19a)$$

derives, where $\bar{\imath}(s)$ is the transform of the applied programmed current and $\bar{S}(s)$ is the "system transform,"[12] obtained from the solution of Fick's equations.

For the case in which the oxidation of species B yields A, *e.g.*, the case of the nitrosophenols, so that $n_1 = n_3$, the boundary conditions that hold on current reversal are (5a) (reduction of C continues at potentials where B is being oxidized), (6a), and

$$n_1(\partial C_B/\partial x)_{x=0} - n_2(\partial C_C/\partial x)_{x=0} = -i/FD \quad (20a)$$

Combination of (20a) and (6a) yields

$$n_1(\partial C_A/\partial x)_{x=0} + n_2(\partial C_C/\partial x)_{x=0} = i/FD \quad (21a)$$

which is the same as (7a). Therefore the same set of equations holds during reversal, and $\bar{C}_B(0, s)$ at any time is given by

$$\bar{C}_B(0, s) = \bar{\imath}(s)\frac{\rho}{n_2FD^{1/2}}\left[\frac{1}{(s + k)^{1/2} - \rho s^{1/2}}\right] \quad (22a)$$

For current reversal, assuming a constant applied forward current density, i

$$i(t) = i + S_{\tau_1}(t)(-Ri) \quad (23a)$$

where $R = (i + i_r)/i$, i_r is the constant applied reverse current density, and $S_{\tau_1}(t)$ is the step function

$$S_{\tau_1}(t) = 0 \qquad t < \tau_1$$

$$S_{\tau_1}(t) = 1 \qquad t > \tau_1$$

The Laplace transform of (23a) is

$$\bar{\imath}(s) = (i/s)[1 - R\exp(-\tau_1 s)] \quad (24a)$$

Combining (19a) and (24a) and inverse transformation of the result yield an expression for $C_B(0, t)$ any time, t, before or after current reversal.

$$C_B(0, t) = g(t) - S_{\tau_1}(t)Rg(t - \tau_1)$$

where

$$g(t) = \frac{i\rho}{n_2FD^{1/2}}L^{-1}\left\{\frac{1}{s[(s + k)^{1/2} - \rho s^{1/2}]}\right\} = \frac{i\rho}{n_2FD^{1/2}(1 - \rho^2)}\left\{\frac{2\rho}{(a\pi)^{1/2}}\exp(-at)\Phi[(at)^{1/2}] + \frac{k^{1/2}}{a}\operatorname{erf}[(kt)^{1/2}] + \frac{2(a - k)^{1/2}}{a\pi^{1/2}}\exp(-at)\Phi[(a - k)^{1/2}t^{1/2}]\right\} \quad (25a)$$

where $a = k/(1 - \rho^2)$, $\Phi(x) = \int_0^x \exp(\mu^2)d\mu$, and erf is the error function. At $t = \tau_1 + \tau_2$, $C_B(0, t) = 0$, and solution of (25a) under these conditions yields τ_2/τ_1 as a function of $k\tau_1$.

Current Reversal, $n_1 \neq n_3$. When oxidation of species B yields another species, E (with a different number of electrons involved in this oxidation than in the reduction of A), *e.g.*, the case of nitrophenols, (20a) is replaced by

$$n_3(\partial C_B/\partial x)_{x=0} - n_2(\partial C_C/\partial x)_{x=0} = -i_r/FD \quad (26a)$$

so that different boundary conditions apply during the forward and reverse reactions. Let $i_{j_f}(t)$ and $i_{j_r}(t)$ represent the instantaneous current involved in the production or consumption of the jth species during forward and backward reaction, respectively, so that

$$i_{B_f}(t) = n_1 FD(\partial C_B/\partial x)_{x=0} \quad (27a)$$

$$i_{B_r}(t) = n_3 FD(\partial C_B/\partial x)_{x=0} \quad (28a)$$

During forward reaction, from (8a)

$$i_C(t) - i_{B_f}(t) = i_f \quad (29a)$$

During reverse reaction, from (26a)

$$i_C(t) - i_{B_r}(t) = i_r \quad (30a)$$

Defining ϕ as previously, eq 10a, differentiating with respect to x, at $x = 0$, and using (29a) yield during the forward reaction

$$FD(\partial\phi/\partial x)_{x=0} = i_{B_f}(t)/n_1 + i_f/n_2 + i_{B_f}(t)/n_2 \quad (31a)$$

During reverse reaction, using (30a), one obtains

$$FD(\partial\phi/\partial x)_{x=0} = i_{B_r}(t)/n_3 + i_r/n_2 + i_{B_r}(t)/n_2 \quad (32a)$$

To obtain an equation which holds during both forward and reverse reactions, so that τ_2 can be obtained in terms of τ_1 through the use of the step-function principle, (31a) and (32a) are combined to yield

$$FD(\partial\phi/\partial x)_{x=0} = i_f/n_2 + i_{B_f}(t)/\rho n_1 - S_{\tau_1}(t) \times \\ \{i_f/n_2 + i_{B_f}(t)/\rho n_1 - i_r/n_2 - i_{B_r}(t)/\rho' n_3\} \quad (33a)$$

where $\rho = n_2/(n_1 + n_2)$, $\rho' - n_2/(n_2 + n_3)$, or, with $i_R = Ri$, and $i_f = i$

$$FD(\partial\phi/\partial x)_{x=0} = [1 - RS_{\tau_1}(t)]i/n_2 + \\ [1 - S_{\tau_1}(t)]i_{B_f}(t)/\rho n_1 + S_{\tau_1}(t) i_{B_r}(t)/\rho' n_3 \quad (34a)$$

Similarly $(\partial C_B/\partial x)$ can be written

$$FD(\partial C_B/\partial x)_{x=0} = i_{B_f}(t)/n_1 + \\ S_{\tau_1}(t)[i_{B_r}(t)/n_3 - i_{B_f}(t)/n_1] \quad (35a)$$

The procedure now follows that for solving for the forward transition time, solution of (34a) and (35a) in the transform plane, finally yielding an expression for $C_B(0, t)$. The Laplace transformation of (35a) is

$$FD(\partial\bar{C}_B/\partial x)_{x=0} = \bar{i}_{B_f}(s)/n_1 + \exp(-\tau_1 s)\bar{I}_{B_r}(s, \tau)/n_3 - \\ \exp(-\tau_1 s)\bar{I}_{B_f}(s, \tau)/n_1 \quad (36a)$$

where

$$\bar{I}_B(s, \tau) = \int_0^\infty \exp(-s\theta) i_B(\theta + \tau)\, d\theta = \\ L[i_B(\theta + \tau)] \quad (37a)^{25}$$

Similarly the transform of (34a) is

$$FD(\partial\bar{\phi}/\partial x)_{x=0} = [1 - Re^{-\tau_1 s}]i/n_2 s + \bar{i}_{B_f}(s)/\rho n_1 - \\ \exp(-\tau_1 s)\bar{I}_{B_f}(s, \tau)/\rho n_1 + \exp(-\tau_1 s)\bar{I}_{B_r}(s, \tau)/\rho' n_3 \quad (38a)$$

Solving (11a) using (13a) and (38a) as boundary conditions and noting that (5a) holds yield

$$-FD^{1/2}\bar{C}_B(0, s) = \{[1 - Re^{-\tau_1 s}]i/n_2 s + \\ \bar{i}_{B_f}(s)/\rho n_1 - \exp(-\tau_1 s)\bar{I}_{B_f}(s, \tau)/\rho n_1 + \\ \exp(-\tau_1 s)\bar{I}_{B_r}(s, \tau)/\rho' n_3\}s^{-1/2} \quad (39a)$$

Similarly solving (2a) with (4a) and (36a) as boundary conditions yields

$$-FD^{1/2}\bar{C}_B(0, s) = (s + k)^{-1/2}\{\bar{i}_{B_f}(s)/n_1 - \\ \exp(-\tau_1 s)\bar{I}_{B_f}(s, \tau)/n_1 + \exp(-\tau_1 s)\bar{I}_{B_r}(s, \tau)/n_3\} \quad (40a)$$

The final equation results from simultaneous solution of (39a) and (40a) to obtain an expression for $\bar{I}_{B_r}(s, \tau)$, substitution of that expression, with expression for $\bar{i}_{B_f}$ and $\bar{I}_{B_f}(s, \tau)$ into (40a) and taking the inverse transform to find $C_B(0, t)$. However, leaving $\bar{I}_{B_f}(s, \tau)$ in its exact form results in fairly intractable integrals on inverse transformation, and it was convenient to use $\bar{i}_{B_f}(s)$ as an approximation for $\bar{I}_{B_f}(s, \tau)$. The range of applicability of this approximation is being investigated and will be discussed in a future communication. With this approximation (39a) and (40a) become

$$-FD^{1/2}\bar{C}_B(0, s) = s^{-1/2}\{[1 - R\exp(-\tau_1 s)]i/n_2 s + \\ [1 - \exp(-\tau_1 s)]\bar{i}_{B_f}(s)/\rho n_1 + \exp(-\tau_1 s) \times \\ \bar{I}_{B_r}(s, \tau)/\rho' n_3 \quad (41a)$$

$$-FD^{1/2}\bar{C}_B(0, s) = (s + k)^{-1/2}\{[1 - \exp(-\tau_1 s)] \times \\ \bar{i}_{B_f}(s)/n_1 + \exp(-\tau_1 s)\bar{I}_{B_r}(s, \tau)/n_3\} \quad (42a)$$

Using (41a) and (42a) to obtain $\bar{I}_{B_r}(s, \tau)$, substituting this value in (42a) and using (16a) ($\bar{i}_{B_f} = -\bar{i}_A$) yields the equation for $\bar{C}_B(0, s)$

$$n_2 FD^{1/2}\bar{C}_B(0, s) = \frac{i\rho[1 - \exp(-\tau_1 s)]}{s} \times \\ \left\{\frac{1}{(s + k)^{1/2} - \rho s^{1/2}}\right\} + \frac{(1 - R)i\rho' \exp(-\tau_1 s)}{n_3 s} \times \\ \left\{\frac{1}{(s + k)^{1/2} - \rho' s^{1/2}}\right\} \quad (43a)$$

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(25) Equation 37a arises from a straightforward application of the Laplace transformation on $i_B(t)$. In general

$$L\{S_\tau(t)F(t)\} = \int_\tau^\infty \exp(-st)F(t)dt = \exp(-\tau s) \times L[F(t + \tau)]$$

or

$$n_2FD^{1/2}\bar{C}_B(0, s) = \bar{g}(s, \rho) - \exp(-\tau_1 s)\bar{g}(s, \rho) + (1 - R)\exp(-\tau_1 s)\bar{g}(s, \rho') \quad (44a)$$

The inverse transform of (44a) is

$$n_2FD^{1/2}C_B(0, t) = g(t, \rho) - S_{\tau_1}(t)g(t - \tau_1, \rho) + (1 - R)S_{\tau_1}(t)g(t - \tau_1, \rho') \quad (45a)$$

where $g(t, \rho)$ is as given in eq 13 in the text. For $\tau_2 < t < \tau_1$, $S_{\tau_1}(t) = 1$, and eq 12 in the text results.

Electron Spin Resonance Spectra of 9,10-Diphenylanthracene Anion and Cation Radicals

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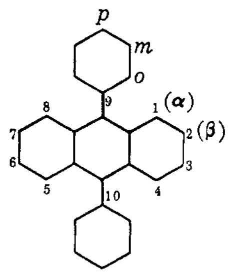
The electron spin resonance (esr) spectra of the 9,10-diphenylanthracene radical anion, prepared by electroreduction in N,N-dimethylformamide, and of the cation, prepared by treatment with concentrated sulfuric acid, are given. The experimental coupling constants are compared with those calculated using Hückel molecular orbital theory assuming different angles between the phenyl rings and the anthracene nucleus.

Recent interest in chemiluminescent[2] and electrochemical[3] reactions of 9,10-diphenylanthracene (DPA) prompted an investigation of anion and cation radicals of DPA. Additional interest in DPA radicals centers on the nonplanarity of the parent molecule caused by interactions of the *o*-hydrogens on the phenyls in the 9 and 10 positions and hydrogens on the anthracene nucleus at positions 1, 4, 5, and 8. By comparing the coupling constants obtained from experimental spectra with those calculated by molecular orbital methods, an estimation of the angle between the phenyl rings and the anthracene nucleus can be obtained.



Brunner and Dörr[4] reported the esr spectrum of DPA anion radical in liquid ammonia at −40°, produced by reaction of DPA with alkali metal. They obtained a 17-line spectrum with a total width of 5.3 gauss and concluded that no conjugation with the phenyl rings occurred and that a very large spin density was present on the 9 and 10 positions. An abstract of a paper mentioning an esr spectrum of DPA radicals has appeared,[5] but details of this work are unavailable.

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