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The Kinetics and Thermodynamics of Transient Equilibria of Reactive Intermediates. I. Theoretical Relationships for the Evaluation of Rate and Equilibrium Constants

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The double potential step chronoamperometry (DPSC) current ratio (R_I)-time(τ) curve due to the generation of an intermediate (B) which participates in a rapidly established equilibrium (i) is

$$2\,B \underset{k_{-i}}{\overset{k_i}{\rightleftharpoons}} B_2 \tag{i}$$

parabolic. The values of the current ratio at the minima, $(R_I)_{min}$, are a direct measure of the equilibrium constants (K_i) for reaction (i). The forward rate constants (k_i) are related to both $(R_I)_{min}$ and τ_{min}, the pulse widths at the minima. Results of theoretical calculations for reaction (i) are presented in the form of polynomial equations. The method of analysis is applicable for K_i ranging from about 10^2 to 10^6 M^{-1} and for k_i ranging from about 5×10^1 to 5×10^7 $M^{-1}s^{-1}$. The theoretical relationships were tested on the known reaction (ii) in DMF with 9-cyanoanthracene (ANCN) concentrations ranging from 0.25 to 2.00 mM. At 288 K,

$$2\,ANCN^{\cdot-} \underset{k_{-ii}}{\overset{k_{ii}}{\rightleftharpoons}} (ANCN)_2^{2-} \tag{ii}$$

K_{ii} was found to be $3.83(\pm0.22)\times10^4$ M^{-1} and k_{ii} was equal to $1.51(\pm0.06)\times10^5$ $M^{-1}s^{-1}$.

A number of reactions of reactive intermediates (B) generated in charge transfer reactions (1) has been observed to follow mechanisms in which the primary step involves either reaction with substrate in a comproportionation equilibrium (2), complexing reversibly with substrate (3) or a reversible monomer-dimer equilibrium (4).

$$A + ne^- \rightleftharpoons B \tag{1}$$

$$B + A \rightleftharpoons 2C \tag{2}$$

$$B + A \rightleftharpoons B(A) \tag{3}$$

$$2B \rightleftharpoons B_2 \tag{4}$$

Pertinent examples of reaction (2) are the $2e^-$ reduction of lucigenin dication to the neutral molecule which undergoes electron transfer with the dication to generate cation radical,[1,2] and the reduction of bianthrone to the dianion which reacts with substrate to produce the anion radical.[3,4] In these reactions, equilibrium (2) is a side reaction which must be taken into account in the study of the irreversible reactions of the primary intermediate (B). Equilibrium (3) has been established to take place upon reduction of SO_2 to the anion radical in aprotic solvents.[5–9] Anthracenes substituted with electron withdrawing groups in the 9 position form anion radicals which participate in equilibrium (4) and the dimer dianions, B_2, are stable in aprotic solvents.[10,11]

The equilibria and associated kinetics have been studied by double potential step chronoamperometry,[1,12] derivative cyclic voltammetry,[4,11] spectroelectrochemistry,[2,3] polarography[5–8] and e.s.r. spectroscopy.[5,6] It has recently been pointed out[9] that the slower techniques such as polarography are not suitable

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for the study of the primary steps in the equilibria since the reactions are generally very rapid. The most suitable transient techniques for the study of the equilibria are double potential step chronoamperometry (DPSC), derivative cyclic voltammetry (DCV) and spectroelectrochemistry. DPSC and spectroelectrochemistry are most readily treated theoretically since much less computer time is necessary to simulate step experiments than is required in the sweep methods such as DCV. In this paper we will only consider DPSC as the measurement technique and we will be concerned with the reversible dimerization equilibria (4).

The DPSC response for equilibria (4) was first treated by Bezilla and Maloy.[13] They were concerned with cases in which the dimer, B_2, undergoes further irreversible reaction to products. Digital simulation was used in a similar theoretical treatment of the DPSC response for reaction (2) by Ahlberg, Hammerich and Parker.[1] Amatore, Pinson and Savéant[12] have presented calculations for the DPSC response due to equilibrium (4) in the absence of further reactions.

The pertinent experimental observation which indicates that reaction (4) is reversible is that the DPSC or DCV current ratio decreases with the increasing time-gate of the experiment as expected for an irreversible reaction but goes through a minimum and then increases at longer times. The behaviour was reported during the reduction of 9-cyanoanthracene in DMF using DCV analysis by Hammerich and Parker.[11] Amatore, Pinson and Savéant[12] studied the same reaction by DPSC and observed similar behaviour. In the latter study, both k_5 and K_5 were evaluated by fitting

$$2\ \mathrm{ANCN}^{\cdot -} \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} (\mathrm{ANCN})_2^{2-} \tag{5}$$

experimental DPSC data to theoretical working curves.

It was the purpose of this study to examine theoretical data for the DPSC response to equilibria (4) to attempt to find general relationships for the evaluation of rate and equilibrium constants which avoid the necessity of calculating theoretical working curves for each case observed experimentally. In particular, it was hoped that the kinetic and thermodynamic parameters could be related to magnitudes and position (on the time scale) of the current ratio minima. Relationships which allow for the quantitative determinations of the parameters were found and are reported here.

RESULTS AND DISCUSSION

Theoretical DPSC data. Double potential step chronoamperometry involves stepping the electrode potential from a rest value where no faradaic processes occur to a value where the charge transfer of interest takes place at a diffusion controlled rate.[14] In practice it is convenient to set the potential limits by placing the cyclic voltammetry couple for the forward and back processes in the center of the potential interval. In order to ensure that the charge transfers are diffusion controlled, the limits are usually >200 mV from the respective cyclic voltammetry peaks. The quantity observed is the normalized current ratio R_I which is the current measured at 2τ divided by that at τ where τ is the pulse width of the experiment. Normalization of R_I is achieved by dividing by $1-2^{-1/2}$ which is the theoretical value for Nernstian charge transfer without kinetic complications.

The digital simulation method[15] used for theoretical calculations involved dividing the

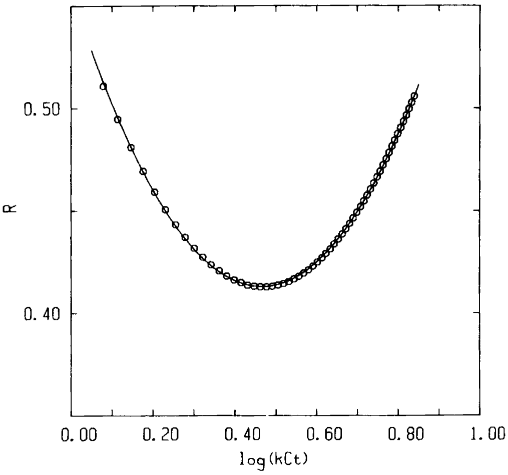

Fig. 1. Theoretical double potential step chronoamperometry data for reversible dimerization reactions. For this curve $\log K_1C_A=1.50$ and $\log k_1C_A=-1.00$.

diffusion layer into J space elements of total thickness limited to 6 $(Dt)^{1/2}$ where D is the model diffusion coefficient (0.45 in this case) and t is the number of time elements and is related to the pulse width. The input for the calculations consisted of τ, expressed as number of time elements, k_4 and k_{-4}. The kinetics were taken into account using finite difference forms of rate equations (6) and (7). For example if $\tau=100$, the

$$-d[B]/dt=2(k_4[B]^2-k_{-4}[B_2]) \quad (6)$$

$$d[B_2]/dt=k_4[B]^2-k_{-4}[B_2] \quad (7)$$

concentrations of A, B and B_2 in the diffusion layer were calculated for each of the 100 time iterations for the forward and the backward steps and R_I was printed. The simulations assume a dimensionless concentration of 1.

Relationships between DPSC parameters and kinetic and thermodynamic constants for the reversible dimerization equilibria. Theoretical working curve data were calculated corresponding to $\log(K_4C_A)$ ranging from 0.000 to 3.000 with $\log(k_4C_A)$ ranging from −1.000 to −3.500. An example of one of the working curves is shown in Fig. 1. The circles are the theoretical data and the solid line is for the best fit to the second order polynomial expression (8). The fit of the data to eqn. (8) is quite good but not exact.

$$R_I=a+b\log(k_4C_A\tau)+c\log(k_4C_A\tau)^2 \quad (8)$$

A much more precise fit is obtained by limiting the R_I values to those close to the minimum. Under the latter conditions, differentiating expression (8) and setting the first derivative equal to zero allows one to calculate both the magnitude of R_I at the minimum, $(R_I)_{min}$, and the value of $\log(k_4C_A\tau_{min})$. The analysis results in $(R_I)_{min}=0.4068$ and $\log(k_4C_A\tau_{min})=0.452$ for the working curve in Fig. 1.

Values of $(R_I)_{min}$ which resulted from the analysis of 25 working curves are summarized in Table 1. The columns marked b are the differences in values of $(R_I)_{min}$ between successive increments of $\log(k_4C_A)$ at a particular value of $\log(K_4C_A)$. What the data reveal is that for each $\log(K_4C_A)$, $(R_I)_{min}$ tend to converge to a single value at small $\log(k_4C_A)$. Furthermore, the convergence takes place in a predictable manner. Each successive b value is approximately 1/3 of the previous one in the horizontal rows. The most extensive calculations were for $\log(K_4C_A)$ equal to 1.000. In this case the successive values of b were; 0.0086, 0.0030, 0.0010 and 0.0003.

The data in Table 2 are values of $k_4C_A\tau_{min}$ obtained from the same calculations. The same trends are observed in this case with $k_1C_A\tau_{min}$ converging to a single value for each $\log(K_4C_A)$ as $\log(k_4C_A)$ was made smaller.

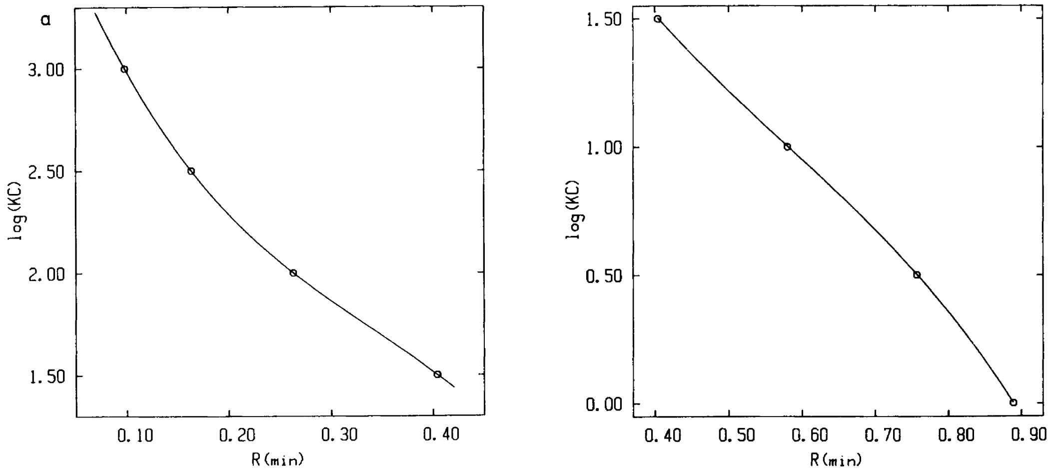

Fig. 2. Theoretical double potential step chronoamperometry equilibrium data for reversible dimerization. Third order polynomial fit to (a), the lower $(R_I)_{min}$ range and (b), the upper $(R_I)_{min}$ range.

Table 1. Theoretical double potential step chronoamperometry equilibrium data for reversible dimerization reactions.[a]

	$R_{\min}$ at $-\log(k_1C_A)$ equal to									
$\log(K_1C_A)$	1.00	[b]	1.50	[b]	2.00	[b]	2.50	[b]	3.00	3.50
3.00	0.0986	0.0001	0.0987		–		–		–	
2.50	0.1632	0.0001	0.1633	0.0001	0.1634		–		–	
2.00	0.2626	0.0001	0.2627	0.0000	0.2627		–		–	
1.50	0.4060	0.0014	0.4046	0.0005	0.4041	0.0002	0.4039		–	
1.00	0.5930	0.0086	0.5844	0.0030	0.5814	0.0010	0.5804	0.0003	0.5801	
0.50	–		0.7754	0.0121	0.7633	0.0040	0.7593	0.0014	0.7579	
0.00	–		–		0.9091	0.0134	0.8957	0.0046	0.8911[c]	0.8897[c]

[a] Data obtained by digital simulation as described in the text. [b] The differences between successive values.[c] The difference between the last two values was 0.0014.

The reason behind the convergence observed in $(R_I)_{\min}$ and $\log(k_4C_A\tau_{\min})$ in Tables 1 and 2 is that the resolution of the simulations increases in going from left to right and down to up in the tables. For example, taking the case where $\log(K_4C_A)$ is equal to 1.000 once more, the number of time elements corresponding to $\tau_{\min}$ were from left to right, 15, 44, 135, 420 and 1325. Thus, in order to find the true $(R_I)_{\min}$ and $\log(k_4C_A\tau_{\min})$ it would be necessary to carry out calculations at even more negative values of $\log(k_4C_A)$. This was not done. Instead, calculations were carried out until successive *b* values were of the order expected for experimental error in the parameters. The true values were obtained by estimation of the values at convergence from the data in Tables 1 and 2. In all cases these differed negligibly from the observed values. Improvements in the computer time necessary for the calculated values to converge could have been made by the use of an implicit rather than explicit finite difference method.[16] Since this would not have affected the accuracy of the results it was deemed to be unnecessary.

The values of $(R_I)_{\min}$ and $\log(k_4C_A\tau_{\min})$ are summarized in Table 3. The numbers in parentheses after those listed for $(R_I)_{\min}$ are the nearest values obtained from the calculations.

Attempts were made to relate $(R_I)_{\min}$ to $\log(K_4C_A)$ and to $\log(k_4C_A\tau)$ by means of third order polynomial equations. In both cases the fit of the data to the curves generated was found to be unsatisfactory for kinetic and thermodynamic analyses. However, in both cases excellent fits of the data to third order polynomial equations were observed when the data were divided into

Table 2. Theoretical double potential step chronoamperometry kinetic data for reversible dimerization reactions.[a]

	$(k_1C_A\tau_{\min})$ at $-\log(k_1C_A)$ equal to									
$\log(K_1C_A)$	1.00	[b]	1.50	[b]	2.00	[b]	2.50	[b]	3.00	3.50
3.00	20.9	0.0	20.9		–		–		–	
2.50	10.9	0.0	10.9	0.0	10.9		–		–	
2.00	5.60	0.00	5.60	0.00	5.60		–		–	
1.50	2.90	0.05	2.85	0.04	2.81	0.01	2.80			
1.00	1.48	0.11	1.38	0.035	1.34	0.01	1.33	0.00	1.33	
0.50	–		0.652	0.052	0.600	0.018	0.582	0.002	0.580	
0.00	–		–		0.263	0.021	0.242	0.010	0.232[c]	0.228[c]

[a] Data obtained by digital simulation as described in the text. [b] The differences between successive values. [c] The difference between the last two values was 0.004.

Table 3. Theoretical double potential step chronoamperometry data for the evaluation of equilibrium and rate constants of reversible dimerization reactions.[a]

$(R_I)_{min}$	$\log(K_1C_A)$	$\log(k_1C_A\tau_{min})$
0.0987 (0.0987)	3.000	1.320
0.1633 (0.1633)	2.500	1.037
0.263 (0.2627)	2.000	0.748
0.404 (0.4039)	1.500	0.446
0.580 (0.5801)	1.000	0.124
0.757 (0.7579)	0.500	−0.237
0.889 (0.8897)	0.000	−0.646

[a] The values at convergence estimated from the data in Tables 1 and 2.

two equal segments. The curves are shown in Fig. 2 (for $\log(KC_A)$ and Fig. 3 (for $\log(k_4C_A\tau_{min})$. The coefficients for the polynomial equations along with the appropriate ranges of $(R_I)_{min}$ are summarized in Table 4.

Application of the theoretical data to an experimental case. The reversible dimerization of 9-cyanoanthracene anion radical, equilibrium (5), has previously been studied in great detail.[10–12] DPSC data obtained from measurements in DMF at 14.8 °C at [ANCN] ranging from 0.25 to 2.00 mM are shown in Fig. 4. The solid lines are those for the corresponding second order polynomial equations best fitting the experimental data (circles). The equations were differentiated and the first derivatives set equal to zero to obtain $(R_I)_{min}$ and τ_{min}. The resulting values of k_4 and K_4 calculated using the relationships in Table 4 are listed in the last two columns of Table 5. The values obtained were

$k_4=1.51(\pm0.06)\times10^5\ M^{-1}s^{-1}$ and

$K_4=3.83(\pm0.22)\times10^4\ M^{-1}$

For both constants, the experimental value deviating furthest from the mean value was that obtained at the lowest substrate concentration, *i.e.* 0.25 mM. This is not surprising since the experimental error is the highest in this case. The results obtained are in accord with those expected from previous work.[11,12]

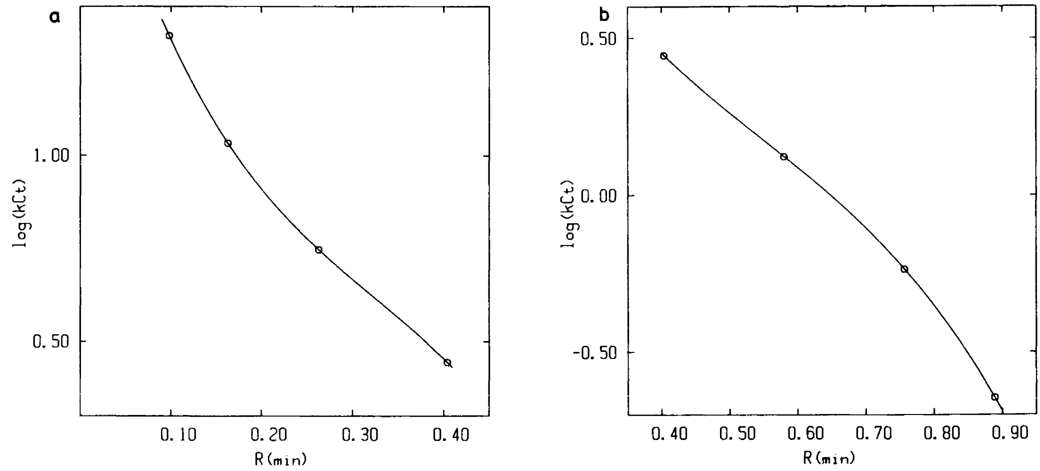

Fig. 3. Theoretical double potential step chronoamperometry kinetic data for reversible dimerization. Third order polynomial fit to (a), the lower $(R_I)_{min}$ range and (b), the upper $(R_I)_{min}$ range.

Table 4. Polynomial coefficients for the calculation of equilibrium and kinetic constants from experimental $(R_I)_{min}$ and τ_{min}.[a]

y^b	$(R_I)_{min}$ Range	*a*	*b*	*c*	*d*
$\log(K_1C_A)$	0.404–0.889	3.82	−9.29	11.42	−6.53
$\log(K_1C_A)$	0.0987–0.404	4.18	−15.00	34.6	−34.3
$\log(k_1C_A\tau_{min})$	0.404–0.889	2.09	−6.98	9.59	−5.85
$\log(k_1C_A\tau_{min}$	0.0987–0.404	1.98	−8.38	19.1	−19.2

[a] The coefficients for the equation $y=a+bx+cx^2+dx^3$, where x is $(R_I)_{min}$ and y is as designated. The lines are shown in Figs. 2 and 3. [b] Defined as in the eqn. above.

Table 5. Experimental double potential step chronoamperometry data for the reversible dimerization of 9-cyanoanthracene anion radical in *N,N*-dimethylformamide.[a]

10^3C_A/M	$(R_I)_{min}$	τ_{min}/s	$10^{-5}k_1/M^{-1}s^{-1}$	$10^{-4}K_1/M^{-1}$
2.00	0.302	0.01552	1.48	3.59
1.00	0.383	0.0200	1.56	3.79
0.50	0.477	0.0260	1.56	3.80
0.25	0.575	0.0378	1.44	4.12
			1.51(0.06)	3.83(0.22)

[a] Measurements in solvent containing Bu_4NBF_4 (0.1 M) at 14.8 °C.

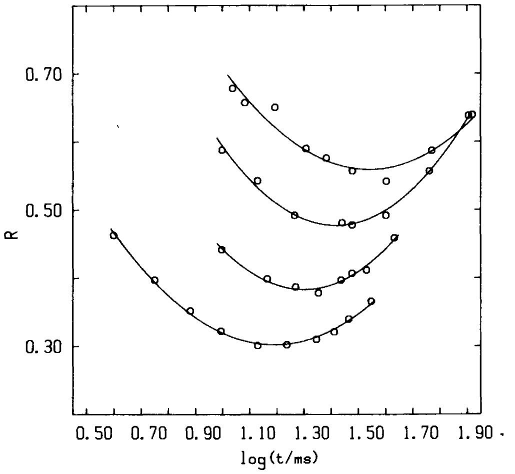

Fig. 4. Experimental double potential step chronoamperometry data for the reversible dimerization of 9-cyanoanthracene anion radical. From top to bottom, [AN−CN] equal to 0.25, 0.50, 1.00 and 2.00 mM in DMF at 14.8 °C.

CONCLUSIONS

Double potential step chronoamperometry data can be related by general equations to the rate and equilibrium constants for reversible dimerization reactions (4). This allows the rate and equilibrium constants to be determined without doing further theoretical calculations. With the minimum value of τ which is experimentally practical taken to be 1 ms and limiting τ to 100 ms with substrate concentrations ranging from 0.1 to 10 mM, the equations presented apply to k_4 ranging from 5×10^1 to 5×10^7 $M^{-1}s^{-1}$ and K_4 ranging from 10^2 to 10^6 M^{-1}. The pertinent experimental parameters, τ_{min} and $(R_I)_{min}$, can be determined to a high degree of precision by taking advantage of the parabolic nature of the response curves and fitting the data to second order polynomial equations.

EXPERIMENTAL

Digital simulation was carried out using a Hewlett Packard 9825A desk computer. Curve fitting was accomplished with the computer interfaced to a Hewlett Packard 9872 Plotter. DPSC experiments were carried out with 600 mV potential steps with the reversible couple for the reduction of ANCN situated near the center of the potential interval. Other experimental and data handling procedures were those previously described.[7]

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