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Theoretical and Experimental Aspects of Electrode Reactions with Coupled Homogeneous Redox Reactions: D. C. and A. C. Polarography*

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We present here a survey of theoretical and experimental studies performed in our laboratories, which deal with influences of homogeneous redox reactions in d. c. and a. c. polarography, with primary emphasis on the latter. These investigations date back to the early 1960's when effects of the catalytic mechanism on a. c. polarography were examined. However, the main thrust in this direction occurred in the past four years when theoretical strategies for handling second order homogeneous reactions coupled to heterogeneous electron transfer were perfected. This development permitted a focused theoretical effort on this topic which encompassed a variety of mechanistic schemes, such as those involving disproportionation, and »nuances« of the consecutive and parallel ECE mechanisms. Experimental results obtained to date satisfactorily support predictions of the theoretical rate laws. One concludes from our studies and parallel efforts in other laboratories that kinetic characteristics of homogeneous redox reactions can substantially influence the polarographic observables under many circumstances. The conclusion follows that kinetic characteristics of homogeneous redox reactions are more broadly accessible *via* polarographic, and other electrochemical relaxation techniques than previously thought. Also, proper care must be taken to account for, or show negligibility of, homogeneous redox reaction effects in studies whose attention is centered on the heterogeneous processes or on multi-component analysis.

INTRODUCTION

Influences of coupled homogeneous redox reactions on electrochemical relaxation technique (ERT) observables have been long-recognized in the context of the so-called first-order catalytic mechanism.[1,2] In this process the reactant in an electrode process is regenerated by an electrochemically inert (at d.c. potentials in question) oxidizing or reducing agent. The simplest mechanistic representation is given by Reaction I (We represent all electrode reactions as reductions, for convenience. See below for notation)

$$A + ne \xrightleftharpoons{E_1^0,\ k_{s,1},\ \alpha} B \qquad (I)$$

$$B \xrightarrow{k_c} A$$

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The first-order catalytic process has served as the basis for numerous homogeneous redox reaction (HRR) rate constant evaluations *via* d.c. polarography and related techniques, and can be used as a »sensitizing« strategy in analytical applications. Indeed, up to the present this mechanism has represented the best known basis for characterizing HRR kinetics *via* ERT.

The disproportionation mechanism, Reaction II,

$$\begin{gathered}\mathrm{A} + n\mathrm{e} \xrightleftharpoons{E_1^0,\, k_{s,1},\, \alpha_1} \mathrm{B} \\ 2\mathrm{B} \xrightarrow{k_2} \mathrm{A} + \mathrm{C}\end{gathered} \tag{II}$$

is another long-recognized, but less frequently encountered example of HRR influences on ERT.[3] Both the catalytic and disproportionation mechanisms are characterized by the fact that a thermodynamically favored heterogeneous charge transfer (HCT) reaction (*e.g.*, electrolysis of the HRR oxidizing agent in the catalytic case) is precluded by very sluggish HCT kinetics. Without the resulting large overpotential, the HRR associated with catalytic and disproportionation mechanisms cannot occur, because reactant concentrations for one or more species involved in the HRR are made negligible in the relevant spacial regions near the electrode-solution interface by the heterogeneous process in question.

Cases where homogeneous redox reactions significantly influence ERT observables under conditions of facile heterogeneous kinetics were given only sporadic attention until the mid-1960's. At that time »nuances« of the consecutive E.C.E. mechanism ($\overrightarrow{\mathrm{E}}$.C.$\overrightarrow{\mathrm{E}}$.),[4-9]

$$\begin{gathered}\mathrm{A} + \mathrm{e} \xrightleftharpoons{E_1^0,\, k_{s,1},\, \alpha_1} \mathrm{B} \xrightleftharpoons[k_4]{k_3} \mathrm{C} + \mathrm{e} \xrightleftharpoons{E_2^0,\, k_{s,2},\, \alpha_2} \mathrm{D}\ (\overrightarrow{\mathrm{E}}.\,\mathrm{C}.\,\overrightarrow{\mathrm{E}}.\ \text{process}) \\ \mathrm{A} + \mathrm{D} \xrightleftharpoons[k_2]{k_1} \mathrm{B} + \mathrm{C}\ (\text{»nuance«})\end{gathered} \tag{III}$$

were recognized as a source of HRR influence on ERT observables, and studied extensively. However, in these efforts HRR kinetic effects were not explicitly investigated in either the relevant theoretical or experimental studies, which were confined to the assumptions of homogeneous and heterogeneous redox reaction equilibria. Subsequently, effects of HRR coupled to the parallel E.C.E. mechanism ($\overrightarrow{\mathrm{E}}$.C.$\overleftarrow{\mathrm{E}}$.-Reaction IV),[10,11]

$$\begin{gathered}\mathrm{A} + \mathrm{e} \xrightleftharpoons{E_1^0,\, k_{s,1},\, \alpha_1} \mathrm{B} \xrightleftharpoons[k_4]{k_3} \mathrm{C} - \mathrm{e} \xrightleftharpoons{E_2^0,\, k_{s,2},\, \alpha_2} \mathrm{D}\ (\overrightarrow{\mathrm{E}}.\,\mathrm{C}.\,\overleftarrow{\mathrm{E}}.\ \text{process}) \\ k_1\end{gathered} \tag{IV}$$

the E.E. mechanism (Reaction V),

$$\mathrm{A} + \mathrm{e} \xrightleftharpoons{E_1^0,\, k_{s,1},\, \alpha_1} \mathrm{B} + \mathrm{e} \xrightleftharpoons{E_2^0,\, k_{s,2},\, \alpha_2} \mathrm{C} \text{ (E. E. Process)}$$

$$\mathrm{A} + \mathrm{C} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2\mathrm{B} \text{ (HRR)} \tag{V}$$

and independent electrode reactions (Reaction VI),

$$\mathrm{A} + \mathrm{e} \xrightleftharpoons{E_1^0,\, k_{s,1},\, \alpha_1} \mathrm{B} \text{ (Electrode Reaction)}$$

$$\mathrm{C} + \mathrm{e} \xrightleftharpoons{E_2^0,\, k_{s,2},\, \alpha_2} \mathrm{D} \text{ (Electrode Reaction)}$$

$$\mathrm{A} + \mathrm{D} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{C} + \mathrm{B} \text{ (HRR)} \tag{VI}$$

were demonstrated to have significant effects on certain ERT observables,[3,12–14] including spectroelectrochemical[12].

With the exception of the first-order catalytic mechanism, none of the foregoing mechanistic schemes had been considered in the context of a.c. polarography by the early 1970's. This observation, our abiding interest in the a. c. polarographic method and the fact that a general approach to developing phenomenological a. c. polarographic rate laws for mechanisms with coupled second (and higher)-order homogeneous chemical reactions had become available, provided us the stimulation to undertake a detailed theoretical--experimental investigation which encompassed the foregoing mechanisms for a. c. polarography. Because suitable solution to the d. c. polarographic boundary value problem is a required step in developing a. c. polarographic rate laws, our activities also have made some contributions to the more extensively examined rate laws for the d. c. polarographic method. The theoretical investigations have incorporated nearly all possible kinetic circumstances, encompassing reversible, quasireversible and irreversible HCT steps, and HRR steps ranging from sluggish to very rapid, without restriction on the homogeneous reaction equilibrium constants. Electrode models include the expanding sphere, as well as simpler approximations to the DME. Extension of the derivational methods to a. c. measurements at stationary electrodes is straightforward[15,16]. Calculational results show in each case that kinetic-mechanistic domains exist where the HRR step can substantially influence the polarographic observables. This not only leads to the conclusion that kinetic characteristics of the HRR are more broadly accessible *via* ERT techniques, such as a. c. polarography, than previously thought, but it also emphasizes that proper care must be taken to account for, or show negligibility of, HRR effects in studies whose attention is centered on other goals, such as heterogeneous redox process characterization, analysis, *etc.* Experimental studies to date have been concerned with a more select group of the foregoing mechanisms. Nevertheless, in all cases studied so far, satisfactory theory-experiment agreement has been realized.

This presentation will survey results of investigations in our laboratory, emphasizing: *(a)* mathematical strategies employed for manipulating the rate laws; *(b)* highlights of predictions of the rate laws for Mechanisms I—VI; *(c)* a survey of experimental results.

STRATEGIES FOR A. C. POLAROGRAPHIC RATE LAW DERIVATIONS

As normally performed[17,18], the a. c. polarographic experiment involves superposition of a small amplitude ($\leq$ 20 mv.) sinusoidal potential on a d. c. potential component whose magnitude is relatively slowly scanned or stepped. The make-up of the electrolyte and electrodes are those normally associated with d. c. polarography or voltammetry. One observes the alternating component of the cell current as a function of the d. c. potential, thus obtaining an »a. c. polarogram.« In kinetic-mechanistic applications, which are of primary concern here, one is interested in both the a. c. amplitude-d. c. potential profile (current amplitude polarogram) and the corresponding phase angle profile (phase angle polarogram) as a function of applied a. c. potential frequency (amplitude and phase angle frequency spectra), so that a typical complete data set defines a four-dimensional profile of amplitude, phase, d. c. potential and frequency. Most measurements focus on the fundamental harmonic response components, but higher (*e. g.*, second harmonics) also are readily characterized and employed for kinetic-mechanistic or assay purposes.[17]

The faradaic component of the a. c. response, extracted from the total cell current by compensation for non-faradaic effects introduced by the electrical double layer and ohmic resistance[17], is significant in potential regions which correspond to the rising portion of an electrode reaction's d. c. polarographic wave. Thus, a. c. polarographic observations are made under conditions of simultaneous flow of direct and alternating current. This has important implications for rate law derivation, as well as data interpretation, which must be recognized. One may think in terms of the d. c. process establishing the mean (or d. c.) surface concentrations of the various reactants, which are then modulated by the a. c. potential perturbation. This viewpoint is quantitatively correct in the small amplitude limit, and qualitatively useful to somewhat larger amplitudes. Because the magnitude of the a. c. response will depend on, among other things, the mean surface concentrations established by the d. c. process, one concludes that the status of the d. c. process in kinetic-mechanistic terms is of considerable consequence in determining the nature of a. c. polarograms. If the d. c. process is influenced by kinetic effects, such as slow HCT or coupled homogeneous chemical reactions (*e. g.*, HRR steps), this necessarily will be reflected in the a. c. response components, regardless of whether or not these rate processes are important on the a. c. time scale. In other words, there is a duality in the a. c. polarographic experiment arising from the simultaneous existence of d. c. and a. c. current flow. For data interpretation and experiment design one must recognize that a dual time scale is operative, one component being the time of observation after initiating electrolysis (the »d. c. time scale«) and the other being the period of the a. c. component (»a. c. time scale«). The implication for rate law derivation is that one must solve both the d. c. and a. c. boundary value problems to obtain a generally useful phenomenological framework. It was established in early investigations[17,19–21] that, in the small amplitude limit (negligible d. c. »faradaic rectification components«[17]), the faradaic d. c. and a. c. boundary value problems are separable. Matsuda[20] introduced the concept of separating the d. c. and a. c. boundary value problem after deriving an integral equation representation of the total faradaic current. The Matsuda approach has been widely applied to mechanisms with first-order chemical reactions coupled to heterogeneous charge transfer (*e. g.*, Mechanism I and Mechanisms III and IV, without the »nuance«)[21–23]. However, with coupled second- or higher-order homogeneous chemimical reactions, reliance solely on the Matsuda technique encounters intractable difficulties, except in special cases. This impasse can be circumvented by separation of the a. c. and d. c. boundary value problems at the differential equation stage, invoking the Gerischer linearization strategy[24] and the Matsuda method to solve the a. c. problem, and utilizing numerical methods, such as Feldberg's digital simulation (the conventional approach[25] and the heterogeneous equivalent[26]), to treat the d. c. problem. This latter approach was employed in our laboratories to derive rate laws for Mechanims II—VI[3,14,23]. Its detailed mathematical features are well-documented[14], and will not be addressed at this time. The important fact to remember is that most of the rate law predictions we will discuss below require the combining of numerical techniques with more classical analytical solution methods to realize the rather general theoretical framework presented.

THE FIRST-ORDER CATALYTIC MECHANISM

The simple, irreversible first-order catalytic mechanism (Mechanism I) was first investigated in the context of a. c. polarography over a decade ago[21]. It has not been a major component of our recent detailed studies of HRR effects in a. c. polarography, but it is discussed here for completeness and to provide a frame of reference for comparing HRR effects observed with other mechanisms.

The first attempt at rate law derivation for Mechanism I provided quantitative predictions and experimental verification only for the fundamental harmonic phase angle contagent[21]. However, subsequent efforts have extended the scope of the rate laws to fundamental harmonic current amplitudes and the second harmonic response[27,28]. As in d. c. polarography, manifestations of the catalytic HRR on the a. c. polarographic observables are predicted to be substantial and distinctive. The phase angle cotangent (cot Φ) frequency spectrum (Figure 1) adopts an unusual feature where cot $\Phi \rightarrow \infty$ ($\Phi \rightarrow 0$) as $\omega \rightarrow 0$. This contrasts to what one observes for most mechanisms where the low frequency cot Φ limiting value is unity[17,19,20]. At sufficiently high frequencies ($\omega >> k_c$), the cot Φ magnitude shows no influence of the HRR and adopts the behavior of the simple single-step redox process, allowing convenient characterization of the HCT rate parameters. The dependences of the fundamental and second harmonic current magnitudes on the HRR rate process are substantial, and the detailed observable-rate parameter (k_c) profiles are functions of the HCT rate constants, k_s and α. Figures 2 and 3 illustrate these remarks. An interesting aspect of the first-order catalytic process is the extreme manner whereby deviations of the a. c. polarograms from their nernstian ($k_s \rightarrow \infty$) shapes, magnitudes, positions, *etc.*, are amplified by increasing the HRR rate constant. In effect, the catalytic HRR places greater demands than simple diffusional mass transport on the heterogeneous step,

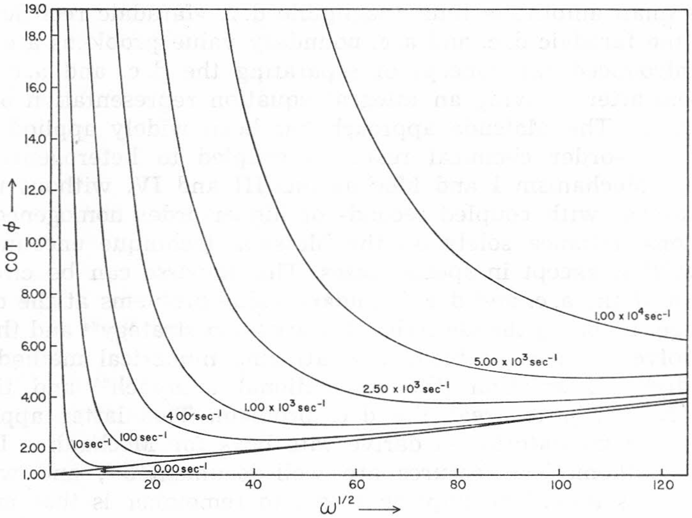


Figure 1. Predicted cotΦ frequency spectrum with first-order catalytic process at $E_{d.c.} = E_{1/2}^r$ with varying k_c.
Parameter Values: $k_s = 0.100$ cm s^{-1}, $\alpha = 0.500$, $D_A = D_B = 1.00 \times 10^{-5}$ cm^2 s^{-1}, $T = 298$ K, n = 1, other parameters have no influence. (From Ref. 21 by courtesy of American Chemical Society)

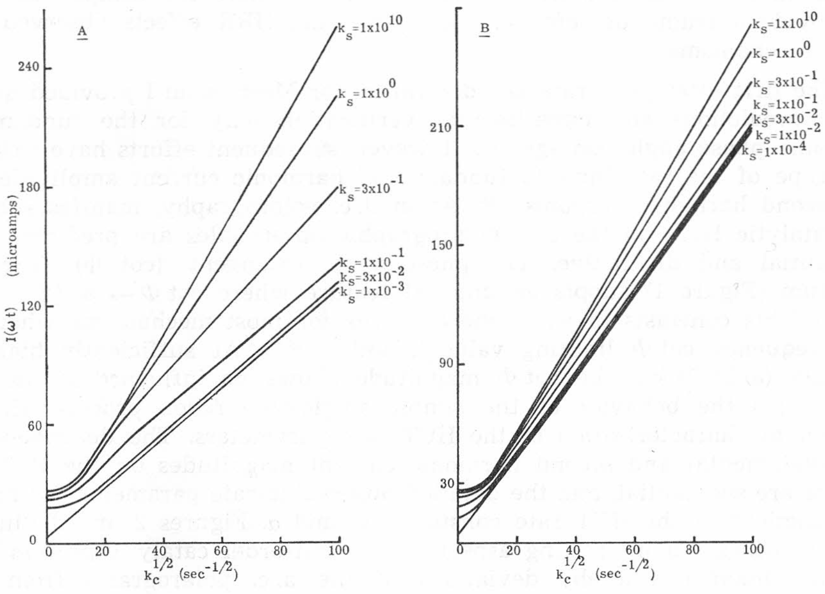


Figure 2. Predicted fundamental harmonic peak current amplitude dependence on k_c.
Parameter Values: n = 1, $T = 298$ K, A = 0.035 cm^2, $\Delta E = 5.00$ mv, $C_o^* = 5.00 \times 10^{-3}$ M, $D_A = D_B = 1.00 \times 10^{-5}$ cm^2 s^{-1}, $\omega = 100$ s^{-1}, $t = 4.00$ s, k_s and k_c values shown on Figure, $\alpha = 0.50$ (A) and 0.80 (B). (From Ref. 27 by courtesy of American Chemical Society)

causing increasing deviations from nernstian behavior with increasing k_c for any finite k_s value[21,27]. This effect can be used as an aid in more readily characterizing very rapid HCT rates. Thus, a catalytic a. c. polarographic wave can be viewed as an opportunity to establish a heterogeneous and/or

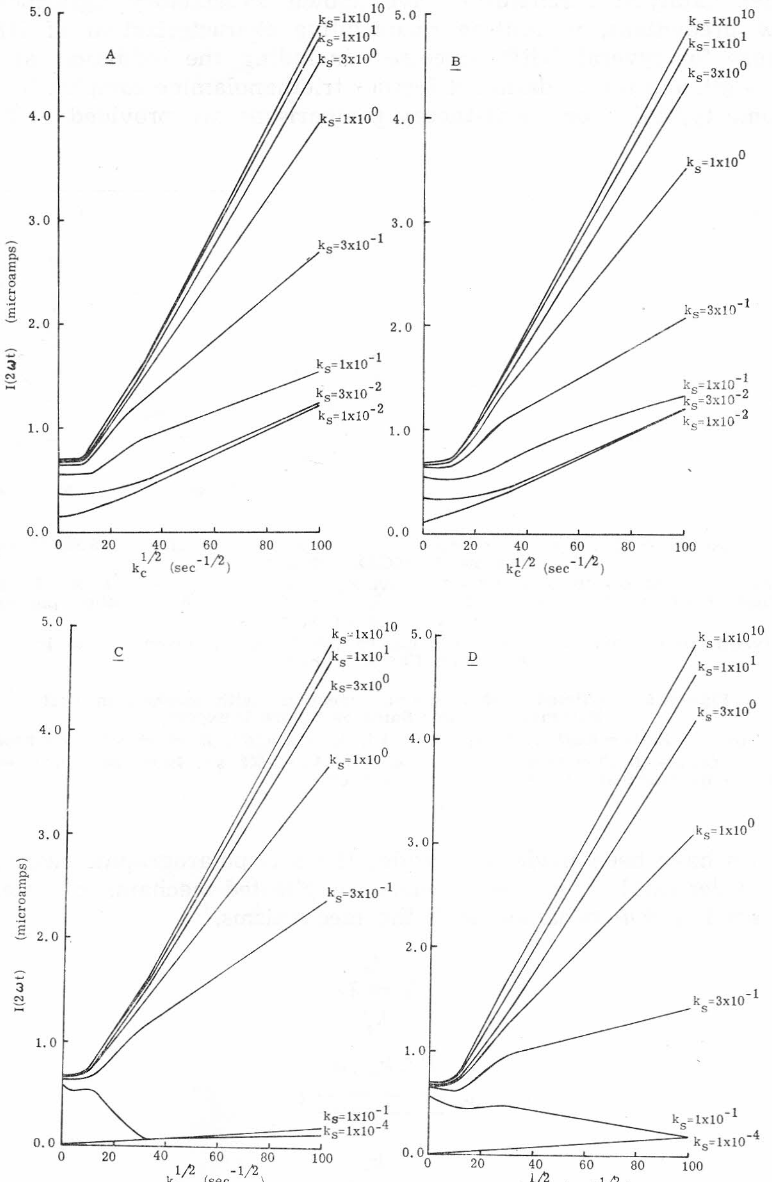
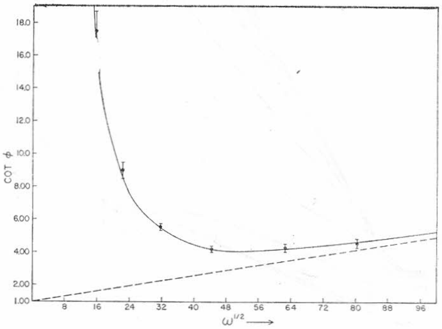


Figure 3. Predicted second harmonic peak current amplitude dependence on k_c Parameter Values: Same as Figure 2, except, $\alpha = 0.50$, negative peak (A); $\alpha = 0.50$, positive peak (B); $\alpha = 0.20$, negative peak (C); $\alpha = 0.20$, positive peak (D). (From Ref. 27 by courtesy of American Chemical Society).

homogeneous redox reaction rate. Studies performed to date indicate that, with the mechanism in question, there should be little difficulty in characterizing from typical a. c. polarographic data both the heterogeneous and homogeneous redox reaction rate parameters, if the rate processes are kinetically significant. To date, experimental a. c. polarographic data obtained on the first-order catalytic mechanism have shown satisfactory agreement with rate law predictions, permitting quantitative characterization of HRR rate parameters for several HRR processes, including the oxidation of Ti^{+3} by chlorate ion[21], and the oxidation of ferrous triethanolamine complex by chlorite icn[27]. Some typical experiment-theory comparisons are provided in Figure 4.



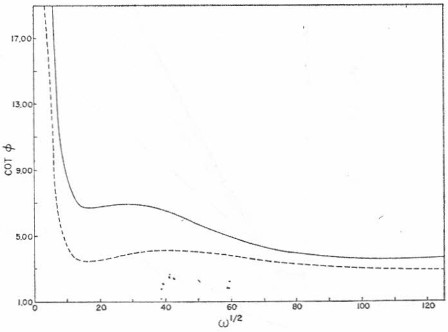


Figure 4. Measured cotΦ frequency spectrum with 0.840×10^{-3} M $TiCl_4$ in 0.200 M $H_2C_2O_4$ and 0.0400 M $KClO_3$ solution.

● = experimental results with $\Delta E = 5.00$ mv, $E_{d.c.} = -0.290$ volt *vs.* S. C. E., $T = 298$ K.

——— = Theoretical curve for $k_c = 1.02 \times 10^3$ s^{-1}, $k_s = 4.6 \times 10^{-2}$ cm s^{-1} other parameters appropriate to system studied.

— — — = results in absence of chlorate ion (no catalytic proces) (From Ref. 21 by courtesy of American Chemical Society).

Figure 5. Predicted cotΦ frequency spectrum with mechanism VIII. Parameter Values: Same as Figure 1, except,

——— $(E_{d.c.} - E_{1/2}{}^{r}) = 0.050$ volt, $k_1 = 5000$ s^{-1}, $k_2 = 50.0$ s^{-1}, $k_3 = 100$ s^{-1}, $k_4 = 0.000$ s^{-1}.

— — — $(E_{d.c.} - E_{1/2}{}^{r}) = 0.070$ volt, $k_1 = 5000$ s^{-1}, $k_2 = 1000$ s^{-1}, $k_3 = 0.000$ s^{-1}, $k_4 =$ s^{-1} (From Ref. 29 by courtesy of Elsevier Publishing Co.)

Efforts have been made to consider the a. c. polarographic response with the first-order catalytic process in more complicated mechanistic contexts than Mechanism I. Cot Φ behavior with the mechanisms,

$$A \underset{k_1}{\overset{k_2}{\rightleftharpoons}} B$$

$$B + ne \xrightarrow[\hspace{2em}]{E_1^0,\, k_{s,1},\, \alpha_1} C$$

and

$$C \xrightarrow{k_3} B$$

$$C \xrightarrow{k_4} A \qquad \text{(VII)}$$

$$A + ne^- \overset{E_1^0, k_{s,1}, \alpha_1}{\rightleftarrows} B$$

$$B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C \qquad \text{(VIII)}$$

$$B \xrightarrow{k_3} A$$

$$C \xrightarrow{k_4} A$$

have been investigated. The studies indicated that the mechanistic perturbations introduced by the additional preceding or following homogeneous chemical reaction are clearly manifested on the cot Φ observable under many conditions (compare Figure 5 to Figure 1). Existing theoretical techniques allow derivation of rate laws for fundamental and second harmonic current amplitudes for any of the common electrode geometries with these mechanisms. However, the effort to effect these advances has not been forthcoming. Generally, little attention has been given Mechanisms VII and VIII for any ERT observable, from either the theoretical or experimental viewpoint, despite the fact that these mechanisms should be occasionally encountered.

THE CASE OF AN HRR COUPLED TO TWO INDEPENDENT ELECTRODE REACTIONS: MECHANISM VI

1. *The Yamaoka Mechanism*

Mechanism VI is a general reaction scheme which involves a number of special cases, including the first-order catalytic mechanism discussed above. However, our interest in considering this reaction scheme in a more general context was initially stimulated by a. c. polarographic observations of Yamaoka[13] in which he observed significant enhancement of a. c. polarographic waves associated with certain reductive electrode processes upon addition of some more easily reduced substances. On the basis of convincing circumstantial evidence provided by a number of examples of this »enhancement« effect, Yamaoka proposed Mechanism VI to explain his observations. The Yamaoka conditions corresponded to the circumstance which is more frequently encountered than catalytic conditions, in the sense that the ordering of the observed polarographic waves is the same as the ordering of the associated thermodynamic redox potentials. That is, if $E_1^0 \gg E_2^0$, then $E_{1/2,1} \gg E_{1/2,2}$. Earlier work[30,31] had considered the effects of Mechanism VI on the d. c. polarographic limiting currents under Yamaoka conditions, but the effects were small, and interest was lost in this origin of a HRR influence for many years.

The implications of enhancement of an a. c. polarographic wave due to more easily reduced depolarizers are profound for analytical applications involving multi-component systems, and for kinetic-mechanistic investigations. Consequently, we decided to attempt the development of a fundamental harmonic a. c. polarographic rate law for Mechanism VI which was as general as possible, encompassing as an important special case the Yamaoka situation. The goal was achieved, with the aid of the theoretical strategies mentioned earlier[14]. The theoretical result was derived for the case where species A and C were initially present in the solution (reductive polarographic waves), and encompassed all combinations of these initial concentrations, heterogeneous and homogeneous rate parameters, and standard potentials (*i. e.* any HRR equilibrium constant). The final results also accommodated diffusion coefficient differences, at least to the extent normally encountered under polarographic conditions. The expanding sphere electrode model was invoked, which provided the expanding plane model as a limiting case. The derivational approach readily accommodates other electrode geometries, if desired.

Fundamental harmonic a. c. polarographic rate law predictions for Yamaoka-type conditions, where the HRR is irreversible, are in qualitative agreement with Yamaoka's original observations. Enhancement of an a. c. polarographic wave upon addition of a more easily reduced substance is predicted *if* the HRR, $A + D \xrightarrow{k_1} B + C$, is sufficiently rapid and *if* the a. c. polarographic wave in question is electrochemically irreversible, or quasi-reversible *in the d. c. sense.* The requirement of sufficient HRR rapidity is self-evident, and was a key to some of Yamaoka's empirical evidence in favor of Mechanism VI[13]. The requirement of slow heterogeneous kinetics also was evident in Yamaoka's empirical results. It also is found that the d. c. component of the rate law predicted significant influence of the HRR on the shape of the rising segment of the d. c. polarographic wave. The influence of the HRR on the irreversible d. c. and a. c. polarographic wave of the more difficultly reduced C/D couple is illustrated in Figure 6.

For the purpose of utilizing the a. c. polarographic wave enhancement to ascertain the magnitude of the HRR rate constant, it was found that the ratio of the a. c. polarographic currents with and without the HRR would provide a simple basis for obtaining k_1 data. The experimental value of this ratio, defined as $R = I(\omega t)_{k_1}/I(\omega t)_{k_1=0}$, is obtained simply by observing the a. c. polarographic wave due to the more difficultly reduced depolarizer (Species C) in the presence and absence of the more easily reduced substance (Species A). Figure 7 illustrates the predicted behavior for this ratio (R-value) under the conditions considered in Figure 6. The R-value *vs.* d. c. potential profile is sigmoidal. Its magnitude at any d. c. potential increases with increasing k_1 until a limiting value is reached. The »limiting value« magnitude is k_1-independent and proportional to the bulk concentration of Species A, C_A^*. The sigmoidal characteristic of the R-value profile is most convenient because the d. c. potential-independent plateau value can be determined with good accuracy without highly precise knowledge of the d. c. potential values. Conveniently implemented working curves relating the plateau magnitude to k_1 values can be developed[14].

Other aspects of the rate law predictions for these conditions indicate that the a. c. polarographic response enhancement phenomenon originates solely in the HRR effect on the d. c. concentration profile. For example, the expression governing R-value profile is frequency independent and contains only terms which are related to the status of the d. c. process [the so-called $F(t)$ terms[17,19]]. Thus, in the Yamaoka mechanism context, the a. c. polarographic response enhancement measurement may be looked upon as a probe into the

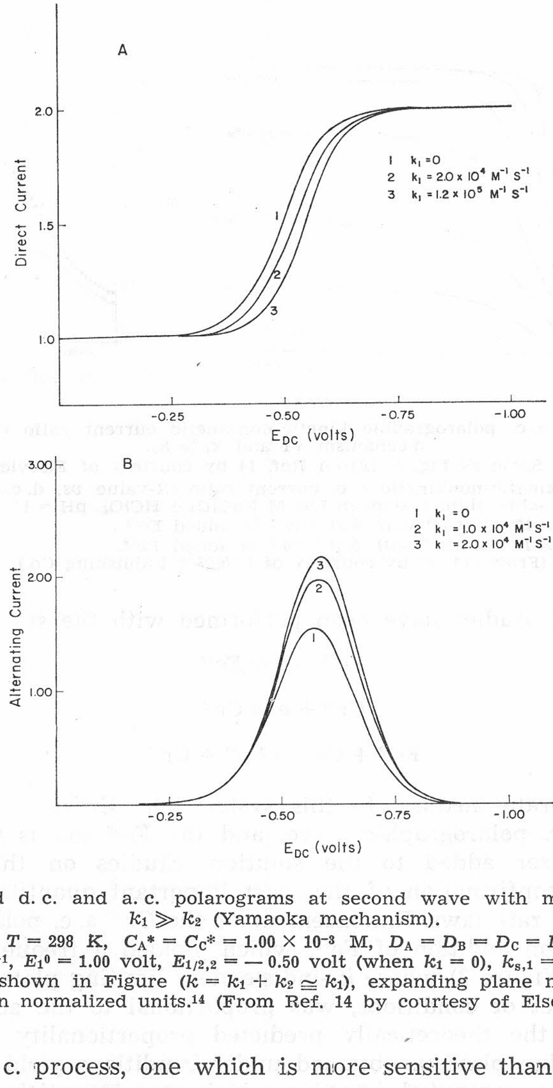
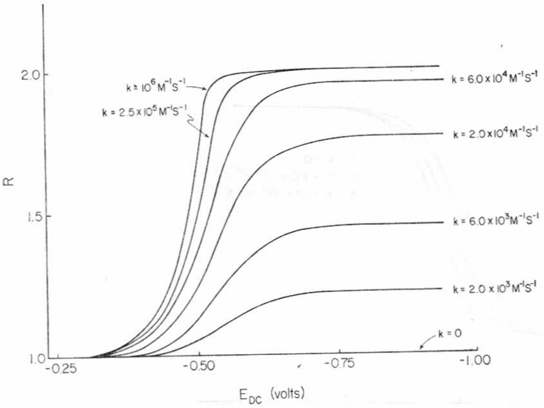


Figure 6. Predicted d. c. and a. c. polarograms at second wave with mechanism VI where $k_1 \gg k_2$ (Yamaoka mechanism).
Parameter Values: $T = 298$ K, $C_A^* = C_C^* = 1.00 \times 10^{-3}$ M, $D_A = D_B = D_C = D_D = 4 \times 10^{-6}$ cm^2 s^{-1}, $t = 1.00$ s., $\omega = 250$ s^{-1}, $E_1^0 = 1.00$ volt, $E_{1/2,2} = -0.50$ volt (when $k_1 = 0$), $k_{s,1} = \infty$, $k_{s'2} < 10^{-6}$ cm s^{-1}, $\alpha_2 = 0.50$, k_1-values shown in Figure ($k = k_1 + k_2 \cong k_1$), expanding plane model, d. c. and a. c. magnitudes given in normalized units.[14] (From Ref. 14 by courtesy of Elsevier Publishing Co.)

status of the d. c. process, one which is more sensitive than the d. c. polarogram itself. The overriding importance of the d. c. process on the *R*-value necessarily implies that this observable will be sensitive to electrode geometry effects[17,19]. Predictions show that the curvature effects associated with the DME are significant, but are readily compensated[14]. The calculations also provide quantitative insights into the influence of the HCT rate constant associated with the observed polarographic wave on one's ability to detect a HRR-induced enhancement. The conclusion that quasi-reversibility in the d. c. sense is a requirement represents the most important qualitative deduction reached. Finally, calculations indicate that accounting for moderate differences in diffusion coefficients associated with the two redox couples is important for computing accurate k_1-values from experimental *R*-value data.



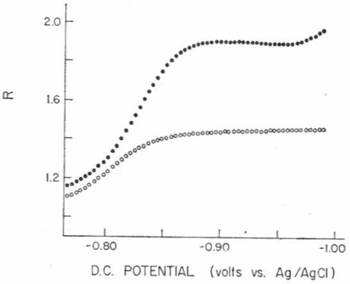


Figure 7. Predicted a. c. polarographic kinetic-nonkinetic current ratio (*R*) at second wave mechanism VI and $k_1 \gg k_2$.
Parameter Values: Same as Fig. 6. (From Ref. 14 by courtesy of Elsevier Publishing Co.)

Figure 8. Measured kinetic-nonkinetic a. c. current ratio (*R*-value *vs.* d. c. potential for iron-chromium system in 1.00 M $NaClO_4 + HClO_4$, pH = 1
● = *R*-value for 5.00×10^{-3} M Cr^{+3} with 5.03×10^{-3} M added Fe^{+3}.
○ = *R*-value for 5.00×10^{-3} M Cr^{+3} with 2.54×10^{-3} M added Fe^{+3}.
(From ref. 32 by courtesy of Elsevier Publishing Co.)

Experimental studies have been performed with the system;

$$Fe^{+3} + e \rightleftharpoons Fe^{+2}$$

$$Cr^{+3} + e \rightleftharpoons Cr^{+2}$$

$$Fe^{+3} + Cr^{+2} \rightarrow Fe^{+2} + Cr^{+3}$$

in acidic perchlorate media[32]. In this system, the Cr^{+3}/Cr^{+2} couple provides the observed a. c. polarographic wave, and the Fe^{+3} ion is the more easily reduced depolarizer added to the solution. Studies on this system have provided initial confirmation of the most important quantitative predictions of the theoretical rate laws. Enhancement of the Cr^{+3} a. c. polarographic wave was observed upon addition of Fe^{+3}, which yielded a frequency-independent *R*-value profile (Figure 8) whose k_1-independent limiting plateau value, observed under one set of conditions, was proportional to the added ferric concentration, with the theoretically predicted proportionality constant. A k_1-dependent *R*-value plateau, obtained under conditions yielding slower HRR kinetics, yielded a computed k_1-value which was in satisfactory agreement with earlier stopped-flow measurements[32].

The scope of application to HRR kinetic measurements of this *R*-value observation under Yamaoka conditions is limited by the fact that the k_1-independent limiting *R*-value is obtained when the HRR is sufficiently fast, setting an upper limit to the measureable k_1 magnitude. This limit corresponds to about 10^5 M^{-1} s^{-1} using the plateau magnitude with millimolar solutions and a normal Hg drop life. The limiting value occurs when the magnitude of the dimensionless parameter, $k_1 C_A{}^* t$ is between 10^2 and 10^3, depending on current measurement accuracy. For good accuracy in computation of k_1, $k_1 C_A{}^* t \leq 100$ is preferred. One concludes that the accessible HRR rate constant magnitudes can be increased by reducing t and/or $C_A{}^*$. The temporal parameter is readily reduced by at least an order-of-magnitude by use of short drop lives[33], or by increasing scan rates if a stationary electrode is employed. The expedient of reducing concentration (below millimolar) is somewhat more limited in the context of fundamental harmonic measurements, primarily because one is dealing with irreversible or nearly irreversible waves in all relevant circumstances, so that the faradaic response magnitudes are quite small, even for normal (millimolar) concentrations. Under such conditions, eliminating faradaic current measurement error arising from double layer charging current, even with phase-sensitive detection methods, becomes rather difficult. For concentrations much below $1—2 \times 10^{-4}$ M, the situation may become intractable, even with the best instrumentation. This difficulty has led us to consider the possibility of using for the purpose at hand second harmonic observations, where double layer charging current contributions are much smaller. It has been established that quite high signal-to-noise ratio data can be obtained by second harmonic a. c. polarographic measurements with totally irreversible electrode processes[34]. These earlier studies indicate that the prospect of using this technique effectively with concentrations even somewhat below 10^{-5} M *with irreversible waves* is promising. Consequently, a second harmonic a. c. polarographic rate law has been derived[35] and examined specifically for Yamaoka conditions. An enhancement of the second harmonic response is predicted under the same conditions where it is observed in the fundamental harmonic case. With a totally irreversible electrode reaction, this second harmonic enhancement is quantitatively *identical* in all respects to that predicted and observed for the fundamental harmonic. That is, an analytical expression is derived for the second harmonic R-value profile which is identical to the fundamental harmonic's. Thus, all working curves, *etc.*, developed for treating fundamental harmonic R-value data, as well as conclusions regarding application scope, are directly applicable to the second harmonic measurement, provided that the a. c. wave is totally irreversible. This identity in behavior disappears when the mechanism is complicated by quasi-reversible heterogeneous kinetics, but in this realm the second harmonic method remains applicable to k_1 evaluation, probably to higher heterogeneous rate constants than possible with the fundamental harmonic response. Experimental studies of the second harmonic response have confirmed the predicted identity of the fundamental and second harmonic R-value profile with irreversible waves, using the iron-chromium system discussed above[35].

Inspection of the theoretical rate law for the HRR effect under Yamaoka conditions suggests that the wave enhancement effect also will be encountered in differential pulse and square wave polarography. Further, with totally irreversible waves, the enhancement should be quantitatively identical (same R-value) to that described above for a. c. polarography. We have confirmed that the enhancement effect exists for the differential pulse method, but the commercial instrument available to us is characterized by instrument time constants which are too large to allow convenient quantitative measurements[35]. Our computerized instrument[36,37] is being adapted to the differential pulse and square wave modes to provide quantitative experimental tests of these predictions.

2. *The Catalytic Mechanism*

Predictions for the catalytic case are deduced from the general rate law for Mechanism VI by inserting the conditions, $E_1^0 \ll E_2^0$ and $E_{1/2,\,2} \gg E_{1/2,\,2}$. This requires using a very small $k_{s,\,2}$-value so that, despite a more positive E^0-value, the electrode reaction, C + e $\rightleftharpoons$ D occurs at a distinctly more negative potential than A + e $\rightleftharpoons$ B (*i. e.*, the polarographic waves are resolved), due to the highly irreversible character of C + e $\rightleftharpoons$ D. The situation is the same as that just considered (Yamaoka conditions) with regard to the relative positions of the polarographic waves due to the reduction of Species A and C. However, the direction of the homogeneous redox reaction is reversed ($k_2 \gg k_1$). Unlike the Yamaoka case, the status of the first polarographic wave is influenced by the homogeneous redox reaction, the attendant wave enhancement being the wellknown catalytic effect[1,2,21,27]. With the specified conditions, the theoretical rate law encompasses in the context of the catalytic case all conceivable situations, including second-order and pseudo first-order homogeneous reactions, the case of reversible homogeneous reactions (next section), all possible kinetic states for the first HCT step, and all within the framework of an

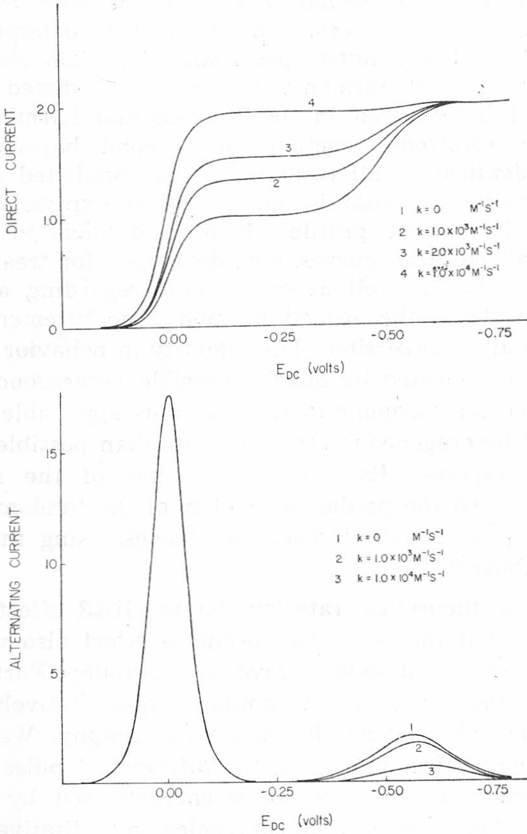


Figure 9. Predicted d. c. and a. c. polarograms with mechanism VI where $k_1 \ll k_2$ (second-order catalytic conditions).

Parameter Values. Same as Figure 6, except $E_1^0 = 0.000$ volt, $E_{1/2,2} = -0.50$ volt (when $k_2 = 0$), $k_{s,1} = \infty$, $k_{s,2} < 10^{-6}$ cm s^{-1}, $\alpha_2 = 0.50$, k_2-values shown in Figure ($k = k_1 + k_2 \cong k_2$), expanding plane model, d. c. and a. c. magnitudes given in normalized units[14]. (From Ref. 14 by courtesy of Elsevier Publishing Co.)

expanding sphere electrode model, with the expanding plane approximation represented as a limiting case.

Some calculated d. c. and a. c. polarograms for conditions where the homogeneous redox reactions are second-order ($C_A^* = C_C^*$) are shown in Figure 9. Most of the qualitative effects are as expected. Increasing k_2 enhances the first *d. c.* polarographic wave at the expense of the second. Disappearance of the second wave will occur if k_2 is increased sufficiently whenever $C_A^* \geq C_C^*$. The suppression of the second a. c. polarographic wave also is an anticipated result. The insensitivity of the first a. c. polarographic wave to k_2 has been explained[14], and is seen to be a result of a special (but not unusual) set of circumstances where d. c. nernstian conditions are combined with comparable bulk concentrations of Species A and C, and $k_2 \ll \omega$. Under different conditions, an enhancement of the first a. c. polarographic wave is predicted, as is familiar with the first-order limit discussed above[21,27].

One finds that the R-value profiles suggested for quantitative data analysis under Yamaoka conditions also are applicable at the second a. c. wave under second-order catalytic conditions. In the catalytic case the HRR causes R to fall below unity, as illustrated in Figure 10.

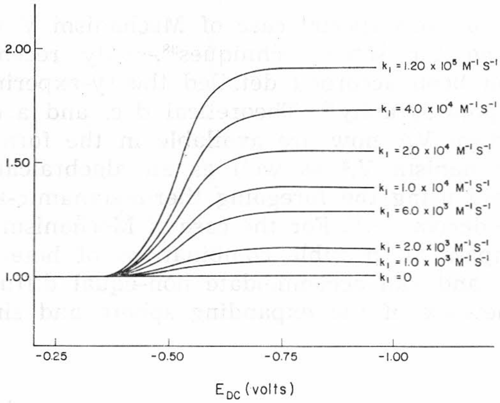


Figure 10. Predicted a. c. polarographic R-values at second wave with mechanism VI and $k_1 \ll k_2$.
Parameter Values: Same as Figure 9. (From Ref. 14 by courtesy of Elsevier Publishing Co.)

3. *Intermediate Cases*

Within the general context of Mechanism VI, the Yamaoka and catalytic mechanisms represent special cases which are characterized by two well-resolved polarographic waves and an irreversible HRR. Other more complicated situations which involve reversible HRR and/or unresolved polarographic waves also are encompassed by the theoretical rate laws in question. The case of a reversible HRR with resolved waves ($E_1^0 \simeq E_2^0$, but $E_{1/2,\,1} \gg E_{1/2,\,2}$ because of small $k_{s,2}$) has been examined in some detail[14]. It has been found that the R-value profiles provide the basis for establishing the magnitudes of k_2 and k_1 under many conditions. Situations where waves are unresolved have been scrutinized briefly[14]. Further discussion of these special situations would be lengthy, and would exceed the time limits for this presentation. For the present, it should be recognized that rate laws are available to assist in d. c. and a. c. polarographic data interpretation, should such »intermediate cases« be encountered.

THE CASE OF A HRR COUPLED TO THE E.E. MECHANISM: MECHANISM V

1. *Irreversible Disproportionation*

The case where the intermediate, B, in the E. E. Mechanism is thermodynamically unstable ($E_1^0 \ll E_2^0$) and the second HCT step is sufficiently irreversible that, despite a more positive E^0-value, it ensues at d. c. potentials negative of the first step ($E_{1/2,1} \gg E_{1/2,2}$) represents the best-known example of Mechanism V. Under these conditions the HRR corresponds to irreversible disproportionation ($2B \rightarrow A + C$) and its effects on the first reduction step under these conditions have been widely studied for a variety of techniques, including d. c. polarography[3]. This special case of Mechanism V usually is represented by the reaction scheme

$$\begin{array}{c} A + e \xrightleftharpoons{E_1^0,\, k_{s,1},\, \alpha_1} B \\ \\ 2B \underset{k_2}{\rightarrow} A + C \end{array} \qquad \text{(VA)}$$

Although studies on this special case of Mechanism V were initiated nearly three decades ago for some techniques[38], only recently has irreversible disproportionation been accorded detailed theory-experiment scrutiny in the context of a. c. polarography[39]. Theoretical d. c. and a. c. polarographic raw laws for Mechanism VA now are available in the form of the general formulation for Mechanism V,[3] as well as an algebraically simpler rate law which was derived using the foregoing thermodynamic-kinetic restrictions at the outset of the derivation[39]. For the case of Mechanism VA these theoretical rate laws encompass all possible combinations of heterogeneous and homogeneous kinetics, and can accommodate non-equal diffusion coefficients[3], all within the framework of the expanding sphere and simpler models of the DME.

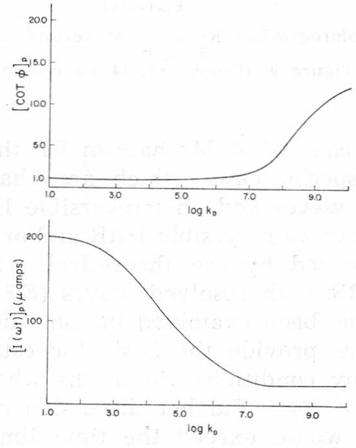


Figure 11. Example of predicted peak current amplitude and cotΦ *vs.* log k_2 profiles for irreversible disproportionation conditions (mechanism VA).
Parameter Values: Same as Figure 2, except $k_{s,1} = \infty$, $\omega = 942\ s^{-1}$, $t = 6.00$ s, k_2-values indicated on Figure, expanding sphere model with sphericity $(Dt/r_o) = 0.68$. (From Ref. 39 by courtesy of Elsevier Publishing Co.) ($k_D = k_2$)

Predictions of these rate laws for Mechanism VA (first wave) show that, with other parameters held constant, the a. c. polarographic current amplitude response is decreased and the phase angle cotangent is increased by increasing the disproportionation rate constant. Figure 11 illustrates this point for the peak current amplitude and its associated cot Φ. It is interesting to note in Figure 11 that the regions of greatest sensitivity to k_2 are distinctly different for the two observables in question. This represents one of many examples of the complementary nature of the current magnitude and phase angle response in a. c. polarographic measurements. Figure 12 provides some examples of the frequency spectrum in a. c. polarographic measurements, using the peak current and its associate cot Φ. Figures 11 and 12 combine to illustrate that the predicted effects of the disproportionation step on the a. c. polarographic observables are substantial, providing sensitive bases for kinetic characterization of this HRR type. The follow-up irreversible disproportionation reaction gives rise to several special effects on the first wave's a. c. observables which are quite unusual for such a relatively simple mechanism (single electron transfer step at d. c. potential of observation, and no adsorption). Specifically, the phase angle cotangent exhibits a temporal dependence, a variation with C_A* and the current amplitude varies nonlinearly with C_A*. These effects are illustrated in Figure 13. It can be shown[39] that the second-order character of the follow-up chemical reactions is the fundamental origin for these distinctive properties. Calculations also show the importance of taking into account electrode sphericity in studies with the DME. This is illustrated in Figure 14.

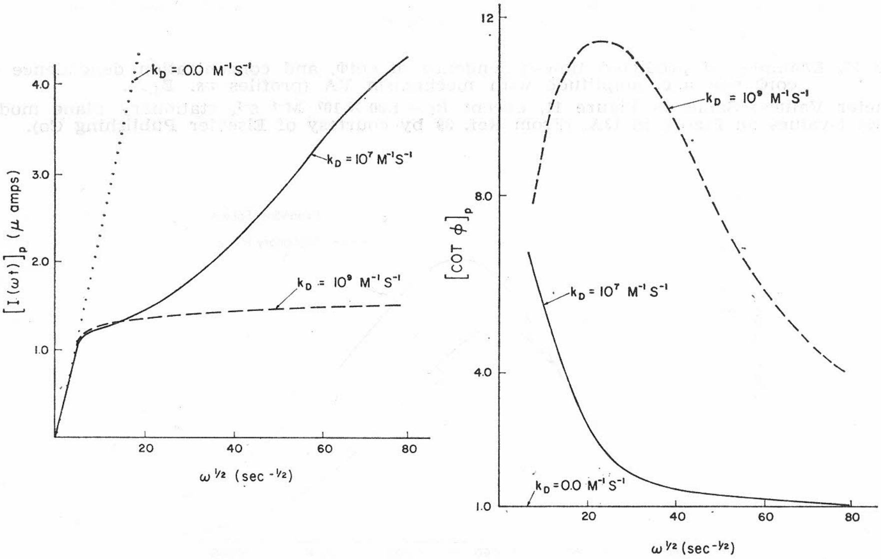


Figure 12. Examples of predicted peak current amplitude and cotΦ spectra for mechanism VA. Parameter Values: Same as Figure 11, except ω-values shown on Figure and stationary plane model. ($k_D = k_2$) (From Ref. 39 by courtesy of Elsevier Publishing Co.)

Experimental investigations with the UO_2^{2+}/UO_2^+ couple in 6 M $HClO_4$ have quantitatively supported the theoretical predictions of the rate laws for Mechanism VA. With this system the a. c. polarographic observables are

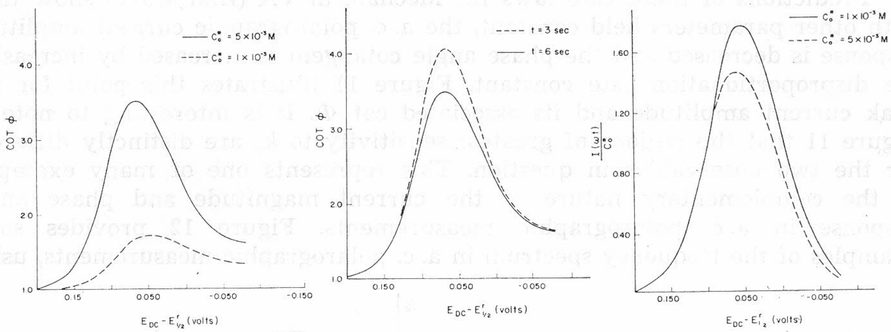


Figure 13. Examples of predicted time-dependence of cotΦ, and concentration dependence of cotΦ and a. c. amplitude with mechanism VA (profiles *vs.* $E_{d.c.}$).

Parameter Values: Same as Figure 11, except $k_2 = 1.00 \times 10^7$ M^{-1} s^{-1}, stationary plane model and *t*-values on Figure in 13A. (From Ref. 39 by courtesy of Elsevier Publishing Co).

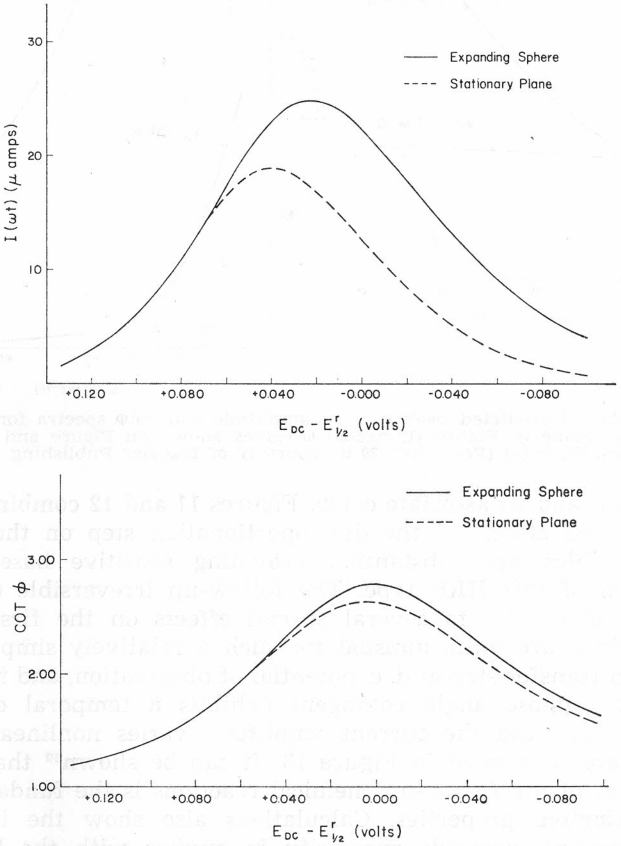


Figure 14. Examples of predicted combined effects of DME drop growth and sphericity on a. c. polarogram and cotΦ polarogram.

Parameter Values: n = 1, $T = 298$ K, $A = 0.0223$ cm², $m = 1.22$ mg s^{-1}, $\Delta E = 10.0$ mv, $C_O^* = 1.00 \times 10^{-2}$ M, $D_A = D_B = 1.6 \times 10^{-5}$ cm² s^{-1}, $k_s = 2.50 \times 10^{-2}$ cm s^{-1}, $\omega = 132$ s^{-1}, $k_2 = 1.40 \times 10^4$ M^{-1} s^{-1}, $t = 7.00$ s, $\alpha = 0.50$, electrode models indicated in figure. (From Ref. 39 by courtesy of Elsevier Publishing Co.)

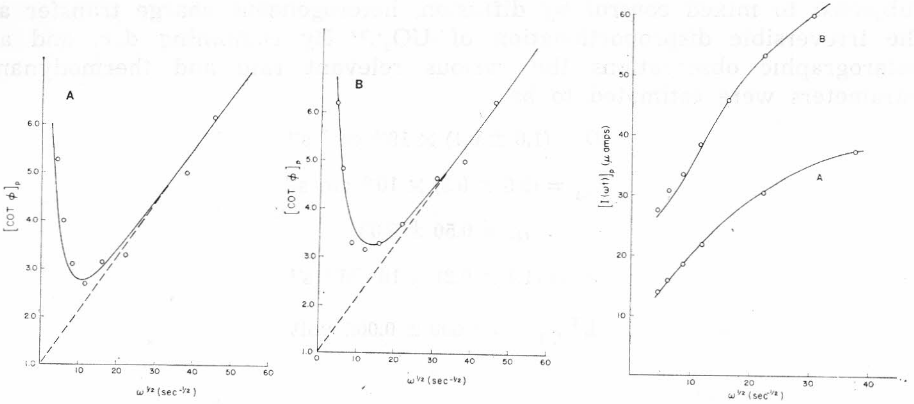
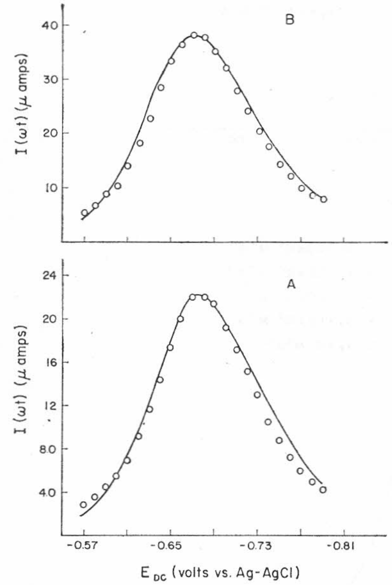


Figure 15. Comparison between experiment and theory for peak cotΦ and peak current amplitude frequency spectra with UO_2^{2+}/UO_2^{+} couple in 6 M $HClO_4$.

○ = Experimental points for 1.0×10^{-2} M UO_2^{2+} (A) and 2.0×10^{-2} M UO_2^{2+} (B) using 10 mv peak-to-peak sine wave and measurement point at 3.50 s after birth of mercury drop ($m = 1.22$ mg s^{-1}), 25 °C.

—— = Theoretical profile for $n = 1$, $T = 298$ K, $m = 1.22$ mg s^{-1}, $\Delta E = 5.00$ mv, $D_A = D_B = 1.6 \times 10^{-5}$ cm^2 s^{-1}, $k_s = 2.5 \times 10^{-2}$ cm s^{-1}, $\alpha = 0.50$, $k_2 = 1.4 \times 10^4$ M^{-1} s^{-1}, $t = 3.50$ s, $C_O^* = 1.0 \times 10^{-2}$ M (A) and 2.0×10^{-2} M (B), Expanding sphere model. (From Ref. 39 by courtesy of Elsevier Publishing Co.)



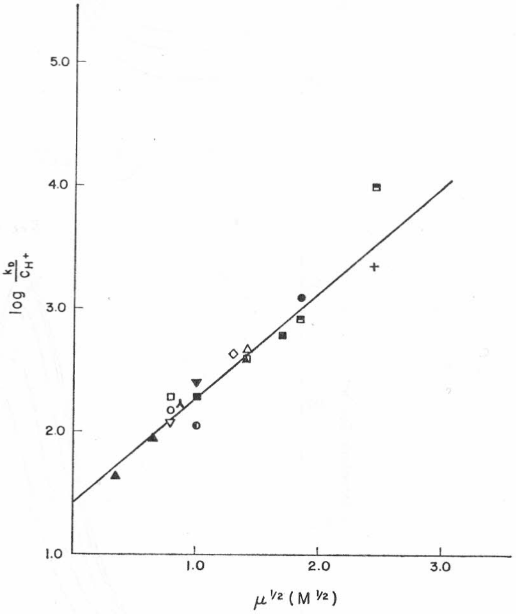


Figure 16. Comparison between theory and experiment for shape of fundamental harmonic a. c. polarograms with UO_2^{2+}/UO_2^{+} couple in 6 M $HClO_4$.

Parameter Values and Notation same as Figure 15. (From Ref. 39 by courtesy of Elsevier Publishing Co.)

Figure 17. Comparison of k_2-values obtained for UO_2^{+2}/UO_2^{+} system by a. c. polarography with those from previous studies.

+ = by a. c. polarography ($k_D = k_2$)

Other symbols represent results of other studies and are defined in Ref. 39. (From Ref. 39 by courtesy of Elsevier Publishing Co.)

subjected to mixed control by diffusion, heterogeneous charge transfer and the irreversible disproportionation of UO_2^+.[39] By combining d. c. and a. c. polarographic observations the various relevant rate and thermodynamic parameters were estimated to be:

$$D = (1.6 \pm 0.1) \times 10^{-5}\ \text{cm}^2\ \text{s}^{-1}$$

$$k_{s,1} = (2.5 \pm 0.2) \times 10^{-2}\ \text{cm s}^{-1}$$

$$\alpha_1 = 0.50 \pm 0.03$$

$$k_2 = (1.4 \pm 0.2) \times 10^{4}\ \text{M}^{-1}\ \text{s}^{-1}$$

$$E^{r}_{1/2,\,1} = 0.690 \pm 0.002\ \text{volt}$$

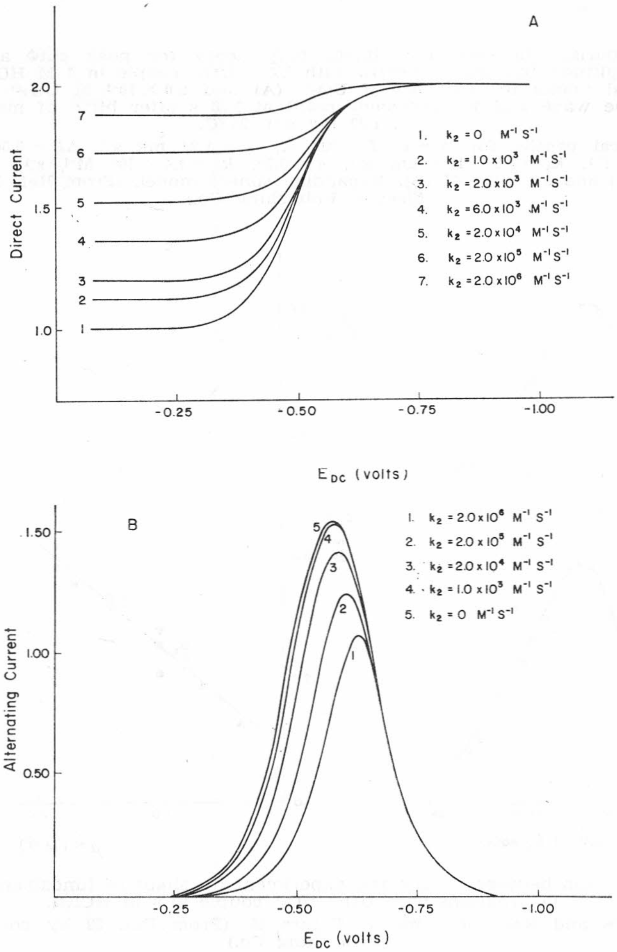


Figure 18. Examples of predicted d. c. and a. c. polarograms at second wave with mechanism V where $k_1 \ll k_2$ (disproportionation conditions).

Parameter Values: Same as Figure 6, except $E_1^0 \ll E_2^0$, $E_{1/2,2} = -5.0$, $k_{s,2} = 1.0 \times 10^{-5}$ cm s^{-1}, $\alpha_2 = 0.50$, k_2-values shown in Figure. (From Ref. 3 by courtesy of Elsevier Publishing Co.)

Theory-experiment comparisons based on these parameters are shown in Figures 15 and 16. The disproportionation rate constant deduced from this study is in good agreement with most electrochemical and non-electrochemical determinations in acid perchlorate media in the sense that this data point lies close to the correlation line between $\log (k_2/C_{H^+})$ and the square root of ionic strength which is applicable to this reaction (see Figure 17)[39].

Unlike most previous developments of the rate laws for irreversible disproportionation, the results deduced from our general theory for Mechanism V, after insertion of the kinetic-thermodynamic restrictions appropriate for irreversible disproportionation, permit prediction of the behavior of the polarographic wave associated with the second reduction step, $B + e \rightleftharpoons C$. As mentioned above, the second wave's HCT is necessarily irreversible. Nevertheless, it is significantly influenced by the disproportionation rate constant in the context of both d. c. and a.c. polarography. Figure 18 provides an illustration. Consequently, when it is observable, the second wave can provide an independent approach to evaluating the disproportionation rate constant.

2. *Irreversible Reproportionation*

The requirement that the intermediate of an electrode reaction be unstable, yet its thermodynamically-favored electrode reaction be precluded by slow HCT at d. c. potentials where $A + e \rightleftharpoons B$ ensues, represents a rather unusual and somewhat demanding combination of circumstances. Consequently, it is not surprising that occurrences of Mechanism VA are rare. Much more likely is the situation where resolved polarographic waves occur by virtue of their thermodynamic properties ($E_1^0 \gg E_2^0$, $E_{1\,2,1} \gg E_{1\,2,2}$) and the favored HRR is the reverse of disproportionation, reproportionation ($A + C \rightarrow 2\,B$). In this instance the HRR can occur only at d. c. potentials corresponding to the second reduction wave ($E_{\text{d.c.}} \approx E_{1/2,2}$), so only these conditions are addressed here. Although reproportionation effects have been considered and exploited in some elegant spectroelectrochemical studies[12], they have been by-and-large ignored with regard to more conventional electrochemical measurements. The inattention paid to effects of reproportionation with conventional electrochemical techniques probably arises for the same reason that the Yamaoka mechanism was ignored for many years of electrochemical progress. Specifically, the belief that these effects will be small or nonexistent was widely held. For example, with several techniques it has been proven for the case where both electrode reactions are nernstian that there will be no effect of homogeneous reproportionation, even if it is reasonably rapid[40]. However, the lessons provided by theoretical and experimental investigations of the Yamaoka mechanism suggested that reproportionation effects might influence observables obtained with an E. E. mechanism under certain conditions. Our investigations with the general theoretical rate law for Mechanism V confirmed these suspicions.

Results of calculations for the situation where polarographic waves were resolved and irreversible reproportionation is the operative HRR were qualitatively analogous to those obtained for so-called Yamaoka conditions with two independent electrode reactions. For example, the predicted polarographic responses at the second wave show no influence of homogeneous reproportionation when the electrode reaction, $B + e \rightleftharpoons C$ is nernstian (reversible) in the

d. c. sense. However, when this electrode process is quasi-reversible or irreversible in the d. c. sense, both d. c. and a. c. responses at the second wave are strongly influenced by a facile reproportionation process. Example of predicted reproportionation effects on d. c. and a. c. polarograms (second waves) are shown in Figure 19. Figure 20 shows plots of the ratio of kinetic

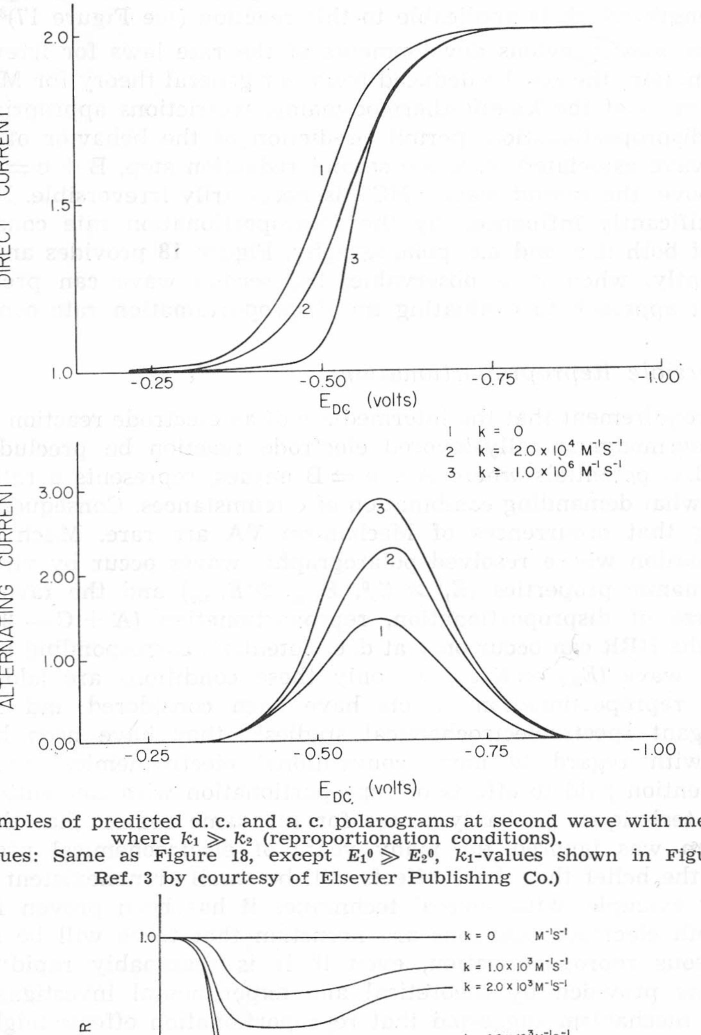


Figure 19. Examples of predicted d. c. and a. c. polarograms at second wave with mechanism V where $k_1 \gg k_2$ (reproportionation conditions).
Parameter Values: Same as Figure 18, except $E_1^0 \gg E_2^0$, k_1-values shown in Figure. (From Ref. 3 by courtesy of Elsevier Publishing Co.)

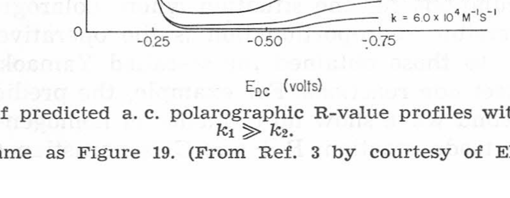


Figure 20. Examples of predicted a. c. polarographic R-value profiles with mechanism V where $k_1 \gg k_2$.
Parameter Values: Same as Figure 19. (From Ref. 3 by courtesy of Elsevier Publishing Co.)

and nonkinetic a. c. currents (the R-value) which were discussed earlier for the Yamaoka mechanism. In the present case the R-value profiles are qualitatively similar to those found for the Yamaoka mechanism, but quantitative identity does not apply. Earlier remarks regarding the practical utility for characterizing a HRR rate constant are applicable in the present case. Experimental characterization of the kinetic-nonkinetic current ratio should be reasonably straightforward in the present context. Observing the »second« polarographic wave with only the stable intermediate, species B, present in the solution bulk provides the nonkinetic current magnitude, $I(\omega t)_{k_1=0}$, since under these conditions species A's presence is excluded and reproportionation cannot occur. The kinetic current magnitude, $I(\omega t)_{k_1}$, is then measured by observing the second polarographic wave with only species A present in the solution bulk.

Experimental studies with the reproportionation mechanism are planned by us, but have not been initiated to date.

3. *Intermediate Cases*

Situations where Mechanism V gives rise to reversible homogeneous redox reactions with resolved waves ($E_1^0 \approx E_2^0$, $E_{1\ 2,1} \gg E_{1\ 2,2}$) have been considered, and methods for evaluating the reproportionation and disproportionation rate constants have been outlined.[3] Similarly, events where the waves due to the two successive heterogeneous steps are not resolved also have been examined. Time does not permit the discussion of these intermediate situations in any detail here, but to illustrate how a HRR can strongly alter polarographic response characteristics in these situations we will consider one special case. Consider the situation where $E_1^0 \gg E^0_2$, but unresolved waves occur because a highly irreversible first heterogeneous step occurs in combination with a relatively facile second heterogeneous process. Under these conditions the direction of the HRR is reproportionation, and its effects on the d. c and a. c. polarographic responses are shown in Figure 21. The effect of the HRR is to make the responses seem more reversible than in its absence. The d. c. polarographic wave is sharpened notably, while the a. c. polarogram is enhanced and narrowed. These predicted effects are readily understood by recognizing that the homogeneous reproportionation process operates in parallel with the first heterogeneous step, providing an alternative mode for conversion of the depolarizer (species A) to the intermediate (species B), the latter being the active species for the facile second heterogeneous step. Consequently, at d. c. potentials where the concentration of species C in the diffusion layer becomes appreciable, the homogeneous step substitutes for the relatively sluggish heterogeneous reduction, $A + e \rightleftharpoons B$, the current due to the second step is increased at the expense of the first, and the polarographic wave properties become more characteristic of the facile second step.

NUANCES OF THE CONSECUTIVE AND PARALLEL E. C. E. MECHANISMS: MECHANISMS III AND IV

Cases where a HRR (»nuance« in this context) is coupled to the consecutive and parallel E.C.E. mechanisms are now recognized to be frequently occuring reaction schemes in electrolytic processes[4–11]. Theoretical rate laws describing manifestations of these mechanisms on d. c. and a. c. polarographic responses

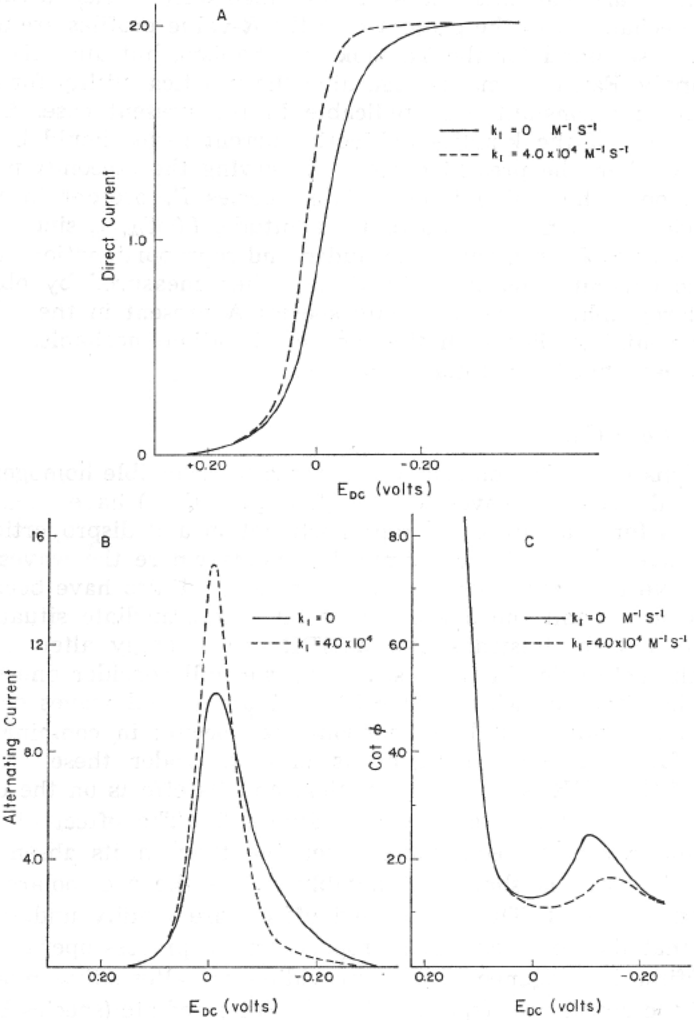


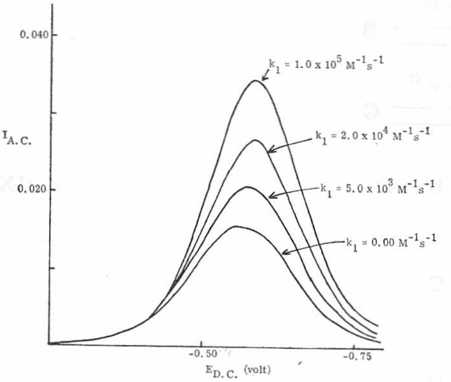
Figure 21. Examples of predicted effects of irreversible reproportionation on d. c. and a. c. polarographic responses with mechanism V and unresolved waves.
Parameter Values: Same as Figure 19, except $E_2^0 = 0.00$ volt, $E_{1/2,1} = 0.00$ volt, $k_{s,1} = 10^{-3}$ cm s^{-1}, $k_{s,2} = 5.0$ cm s^{-1}, and k_1-values shown on Figure. (From Ref. 3 by courtesy of Elsevier Publishing Co.)

have been examined in considerable detail as part of our effort to better understand the role of the HRR in polarographic methods[23]. To date we have focused on the situation where the intervening chemical step in the E.C.E. sequence is first-order, although the derivational procedures can accommodate second-order intervening processes. A generalization of the parallel E.C.E. sequence, which is related to Jacq's »Schema Carre,«[41] also has been studied[23], and is represented by Mechanism IX.

$$
\begin{gathered}
\mathrm{A} + e^- \xrightleftharpoons{E_1{}^0,\ k_{s,1},\ \alpha_1} \mathrm{B} \\
\mathrm{D} + e^- \xrightleftharpoons{E_2{}^0,\ k_{s,2},\ \alpha_2} \mathrm{C} \\
\mathrm{A} + \mathrm{C} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{B} + \mathrm{D} \\
\mathrm{B} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \mathrm{C} \\
\mathrm{A} \underset{k_6}{\overset{k_6}{\rightleftharpoons}} \mathrm{D}
\end{gathered}
\qquad \text{(IX)}
$$

Derivational strategies we have employed allow one to treat these reaction sequences with similar degrees of generality described for the simpler mechanisms discussed above. Clearly, the number of reasonably distinct thermodynamic-kinetic situations one can envision for these multi-step processes is almost infinite. Our studies have been necessarily selective, but the number of conditions considered have been extensive, nevertheless. This observation, together with time limitations and the reader's patience, precludes in this forum anything more than a few remarks encompassing a small fraction of our studies with this mechanistic category. The present discussion will focus on the effects of the HRR, giving negligible attention to the first-order intervening chemical steps. However, it should be recognized that unless the latter are relatively facile, the mechanisms in question would not be operative.

The case of a HRR coupled to a consecutive E.C.E. mechanism (Mechanism III) bears a significant relationship to the independent electrode reaction case (Mechanism VI). In Mechanism III species B and C are coupled through the intervening first-order homogeneous chemical step, $\mathrm{B} \rightleftarrows \mathrm{C}$, whereas with Mechanism VI this reaction is nonexistent. In the E.C.E. case, species C is generated by the intervening chemical step and its presence in the solution bulk is not required, whereas the latter is necessary to observe Mechanism VI. In any case, qualitative similarities between Mechanisms III and VI are to be expected and these expectations are confirmed by the rate law predictions. These similarities are most obvious in the case which is the analog of the Yamaoka mechanism where $E_1{}^0 \gg E_2{}^0$, resolved waves are observed ($E_{1/2,1} \gg \gg E_{1/2,2}$) and the HRR proceeeds irreversibly from left to right as written in Mechanism III ($k_1 \gg k_2$). The operative mechanism at the first wave is the simple follow-up chemical reaction case[42]. As with Mechanism VI, the HRR effects are observable only at the second wave. They enhance the second a. c. polarographic wave, relative to its magnitude in absence of the HRR (Figure 22). Furthermore, the a. c. polarographic *R*-value profile depicting the ratio of the a. c. current magnitude in the presence and absence of the HRR [$R = I(\omega t)_{k_1} / I(\omega t)_{k_1=0}$] is sigmoidal, as with the Yamaoka mechanism (Figure 23). Experimental determination of the R-value profile is not as straightforward as with the Yamaoka mechanism, but it can be made a useful strategy for quantitative kinetic parameter estimation[23]. A final similarity to the Ya-



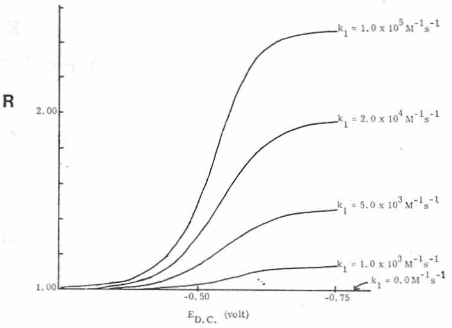


Figure 22. Examples of predicted effects of HRR »nauance« on a. c. polarographic response at second wave with E. C. E. mechanism (mechanism III) where $k_1 \gg k_2$.

Parameter Values: Same as Figure 6, except $k_3 = 10.0$ s^{-1}, $k_4 = 0.00$ s^{-1}, and k_1 values shown on Figure.

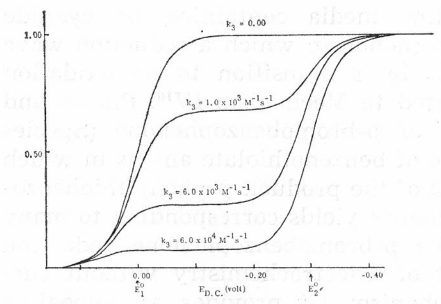
Figure 23. Predicted a. c. polarographic R-value profiles for conditions shown in figure 22.

maoka mechanisms is that the second a. c. polarographic wave's cot Φ value is not influenced by the HRR. On top of these similarities there are some significant qualitative differences between Mechanism III and VI predicted for the conditions in question. For example, the d. c. polarographic limiting current may be influenced significantly by the HRR, and HRR effects on the d. c. and a. c. polarographic wave shapes and magnitudes are predicted to occur even when the second heterogeneous step is nernstian, although the largest effects still are observed when this HCT process is irreversible.

With Mechanism III we also have found significant predicted HRR effects for conditions where $E_1{}^0 \ll E^0{}_2$, but resolved waves are still observed ($E_{1/2,1} \gg \gg E_{1/2,2}$) due to a very sluggish second heterogeneous charge transfer step. Here the direction of the HRR is »backward« ($B + C \rightarrow A + D$). In this case the HRR effect enhances the first d. c. and a. c. polarographic wave magnitudes at the expense of the second wave's magnitudes. This is to be expected because in this situation the HRR proceeds in the vicinity of the first wave, producing »one-half regeneration«[43] of species A in the manner of simple disproportionation, and becoming phenomenologically identical to disproportionation under certain conditions, as when the intervening chemical step is a facile equilibrium. Indeed, many classical experimental examples of the disproportionation mechanism probably proceed by this E.C.E. with »nuance« pathway[44,45]. For the irreversible backward HRR case in question, HRR effects are maximized as a function of k_2, approaching zero when $k_2 \rightarrow 0$ and when $k_2 \rightarrow \infty$. In the case where $E_1{}^0 \ll E_2{}^0$, but the second HCT is facile, the second heterogeneous step proceeds in union with the first, and a single wave is observed. This situation where the product of the intervening chemical reaction, species C, is more easily reduced than the depolarizer, species A, is a frequently-encountered special case of the consecutive E.C.E. mechanism[46,47]. Our calculations show that the HRR has relatively minor or totally negligible effects under these conditions. This is because the rapid heterogeneous process, $C + e \rightleftharpoons D$, tends to suppress the concentration of species C to the extent that the rate of the process $B + C \rightarrow A + D$ becomes negligible.

The parallel E.C.E. mechanism (Mechanism IV) is known to give rise to rather interesting, unique observations when encountered experimentally. Feldberg and Jeftić[10] reported the observation of linear sweep voltammograms of chromicyanide ion in alkaline media containing no cyanide which exhibited the rather disturbing phenomenon in which a reduction wave was followed at more negative potentials by a transition to an oxidation wave. This effect was convincingly attributed to Mechanism IV[10]. Pinson and Saveant[11] reported cyclic voltammograms of *p*-bromobenzophenone (Species A in Mechanism IV context) in the presence of benzenethiolate anions in which the observed cyclic voltammogram was that of the product, *p*-phenylthiobenzophenone (species D). For this system coulometric yields corresponding to many moles per Faraday were observed for the *p*-bromobenzophenone reduction under certain conditions, and the concept of »electrochemistry without current« was introduced[11]. Here again, Mechanism IV provides an appealing explanation of the observations.

Our calculations for Mechanism IV predict similarly interesting effects for d. c. and a. c. polarography. The systems studied in the foregoing experimental work involved conditions where species A is present in the solution bulk, $E_1{}^0 \gg E_2{}^0$ so that the HRR proceeds in the direction $A + C \rightarrow B + D$, and the first heterogeneous charge transfer step is facile ($E_1{}^0 \approx E_{1/2}{}'_1$). Even without a HRR contribution ($k_1 = 0$), under these conditions the parallel E.C.E. mechanism has interesting consequences, which have been long recognized[48]. At potentials where heterogeneous reduction of species A ensues one is in the limiting current region for oxidation of species C. Consequently, except for the trivial limiting case where the $B \rightleftharpoons C$ process it too sluggish to be of consequence, one will observe two polarographic waves. The first wave involves reduction of species A, followed by oxidation of species C to an extent controlled by the $B \rightarrow C$ process. Thus, one has a »mixed current« wave[48]. When sufficiently negative potentials are reached that the $C \rightleftharpoons D + e$ process ceases, ($E_{d.c.} \approx E^0{}_2$ for facile HCT), a transition to a pure $A + e \rightleftharpoons B$ reduction current occurs, yielding a second wave whose shape is characteristic of the $C \rightleftharpoons D + e$ process. The relative magnitude of the two waves depends significantly on the rate of the intervening chemical step, as shown in Figure 24. In principle, if k_3 is sufficiently large, the oxidation and reduction components at the first wave may almost perfectly balance so that the first wave will not be detectable, and the observed polarogram will exhibit only the second wave associated with the second heterogeneous charge transfer. Similar variations are predicted for the a. c. polarograms under these conditions with the pure parallel E.C.E. mechanism. When a significant HRR rate is introduced into the reaction scheme, Species A and C may be reduced and oxidized, respectively, either at the electrode or homogeneously. The effect of the HRR is to significantly suppress the magnitudes of each of the two waves in both d. c. and a. c. polarography. Figure 25 illustrates these effects on the d. c. polarograms, focusing on the second wave and the first wave's limiting current. Suppression of the polarographic responses by the HRR is not surprising, in view of the fact that the HRR provides a homogeneous pathway for reduction and oxidation of species A and C, reducing their availability for electrolytic reduction. In the limit where the two homogeneous steps are extremely rapid, the first wave will disappear completely. The minute, undetectable current



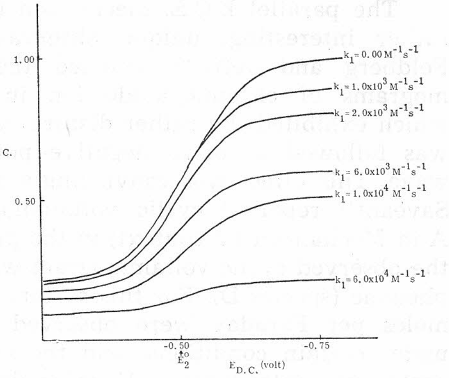


Figure 24. Examples of predicted effects of intervening chemical reaction on d. c. polarograms with »pure« E. C. E. mechanism (mechanism IV with $k = k_1 + k_2 = 0$).
Parameter Values: Same as Figure 6, except $k_{s,1} = k_{s,2} = \infty$, E^0-values, and k_3-values shown in Figure, $k_4 = 0$.

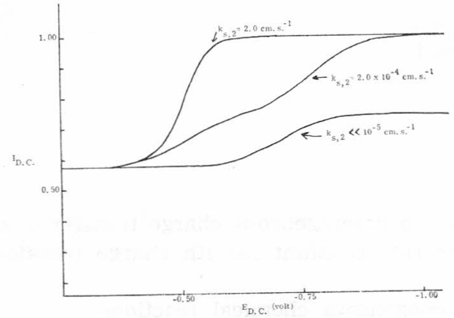
Figure 25. Examples of predicted effects of HRR »nuance« on d. c. polarogram (first wave limiting current and second wave) with E. C. E. mechanism where k_1 k_2.
Parameter Values: Same as Figure 24, except $E_2^0 = -0.50$ and k_1-values shown on Figure.

which flows in the vicinity of the first wave, including its limiting current region, merely plays an initiating role for the chemical processes,

$$A + C \rightarrow D + B$$

$$B \rightarrow C$$

whose net consequence is the *homogeneous chemical* conversion, $A \rightarrow D$. A second polarographic wave *due to reduction of species D* will be the only polarographic response observed under these conditions. Our computations have revealed an additional interesting feature which can occur under the conditions in question if the second heterogeneous step approaches irreversibility in the d. c. sense. Here the second wave is split into two waves, as illustrated in Figure 26 (case where $k_{s,2} = 2.0 \times 10^{-4}$ cm s^{-1}). For these nearly irreversible conditions, cessation of electrolytic oxidation of species C is not followed immediately by electrolytic reduction of species D when the potential is scanned negatively, as is the case with a nernstian $C \rightleftharpoons D + e$ process (case where $k_{s,2} = 2.0$ cm s^{-1}, Figure 26). Instead, one observes two waves instead of one, the first corresponding to elemination species C oxidation and the second due to onset of species D reduction at more negative potentials. The third wave can not occur without formation of species D homogeneously because otherwise termination of species C's electrolytic oxidation would eliminate species D from the reaction media. Thus, the HRR process combined with a slow second heterogeneous step is required for the observation of three waves. Figure 26 also illustrates that third wave can be unobservable if $k_{s,2}$ is sufficiently small that the onset of species D's reduction occurs outside the accessible d. c. potential range ($k_{s,2} \ll 10^{-5}$ cm s^{-1}). This splitting of the second wave into two also is manifested in the a. c. current magnitude polarogram, although it is not apparent in the cot Φ profile (Figure 27).



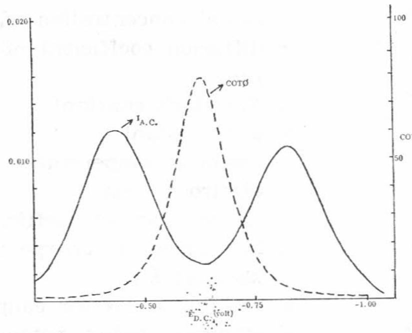


Figure 26. Examples of predicted effects of HCT rate on second d. c. polarographic wave with mechanism IV.

Parameter Values: Same as Figure 25, except $k_1 = 1.00 \times 10^4$ M^{-1} s^{-1}, $\alpha_2 = 0.50$ and $k_{s,2}$-values shown on Figure.

Figure 27. Example of a. c. Polarogram under conditions of Figure 26 where $k_{s,2} = 2.0 \times 10^{-4}$ cm s^{-1}.

CONCLUSIONS

In this presentation we have tried to survey various pathways whereby homogeneous redox reactions can influence d. c. and a. c. polarographic observables, emphasizing recent experimental and theoretical studies performed in our laboratory. The following general conclusions of significance can be drawn from the results presented here.

(a) The pathways whereby HRR effects are manifested on d. c. and a. c. polarographic responses are quite numerous. Probably more opportunities than normally recognized exist for kinetic-thermodynamic characterization of HRR by polarographic methods and for HRR interferences in polarographic measurements with simple objectives, such as analysis.

(b) It is particularly important to recognize that certain coupled HRR mechanisms once though to yield inconsequential effects, such as the Yamaoka mechanism and reproportionation, can substantially alter polarographic observables under appropriate conditions. The a. c. polarographic response in these particular cases provides a previously-unrecognized broad scope of possibilities for kinetic characterization of HRR. With the Yamaoka mechanism the procedures are particularly straightforward and the possibilities for application especially abundant.

(c) Modern mathematical strategies which combine numerical and analytical procedures make tractable general derivation of d. c. and a. c. polarographic rate laws for highly complex mechanism involving combinations of first- and second-order homogeneous chemical reactions coupled to diffusion and heterogeneous charge transfer. The broad scope of heterogeneous and homogeneous kinetic domains accommodated by these procedures fails to encompass only a very few limited situations. The mathematical methods in this field are mature and mathematical intractability seldom can be advanced as a basis for limiting one's data interpretation to casual qualitative conclusions.

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NOTATION

C_i^* = initial concentration of species i

D_i = diffusion coefficient of species i

t = time

F = Faraday's constant

R = gas constant

T = absolute temperature

A = electrode area

α_i = charge transfer coefficient for ith heterogeneous charge transfer step

$k_{s,i}$ = heterogeneous charge transfer rate constant for ith charge transfer step (at E^0)

k_i = rate constants for coupled homogeneous chemical reactions

E_i^0 = standard redox potential for ith charge transfer step (European convention)

E_{dc} = dc component of applied potential

$E_{1/2,i}$ = observed dc polarographic half-wave potentials for ith charge transfer step

$E^r_{1/2,i}$ = reversible dc polarographic half-wave potential for ith charge transfer step

ΔE = amplitude of applied alternating potential

ω = angular frequency of applied alternating potential

$I_{D.C.}$ = dc faradaic current component

$I_{A.C.}$ = faradaic fundamental harmonic current

Φ = phase angle of faradaic fundamental harmonic alternating current relative to applied alternating potential

m = mercury flow rate

r_o = dropping mercury electrode radius

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SAŽETAK

Teorijski i eksperimentalni aspekti utjecaja homogenih redoksreakcija na elektrodne procese. d. c. i a. c. polarografija

I. Ružić, R. J. Schwall i D. E. Smith

Dan je pregled teorijskih i eksperimentalnih istraživanja na polju utjecaja homogenih redoks reakcija na elektrodne procese u d.c. i a.c. polarografiji. Specijalni slučaj takovih reakcija su neke vrste katalitičkih komplikacija koje su već duže vremena bile predmet detaljne analize od strane većeg broja autora. Najveći broj radova posvećen je analizi d. c. polarografskih podataka, a razvijena je nedavno teo-

rijska baza za interpretaciju takovih podataka i u a. c. polarografiji. Na taj način omogućena je interpretacija eksperimenata i predikcija rezultata na osnovi teorije za čitav niz složenih mehanizama kao što su: disproporcionacija, reproporcionacija i ostale katalitičke reakcije, kako za slučaj nekoliko neovisnih elektrodnih procesa, tako i za slučaj višestepenih elektrodnih procesa, te njihovih kombinacija uz neke dodatne homogene interakcije kao što su konsekutivni i paralelni ECE mehanizmi. Eksperimentalni su rezultati do sada pokazali dobro slaganje sa teorijskim predikcijama kao i da postoji značajan mjerljivi utjecaj kinetičkih parametara homogenih redoks reakcija na razne tipove elektroanalitičkih odziva što ranije nije bilo dovoljno poznato. Također iz toga slijedi da je potrebno uzeti u obzir taj mogući utjecaj homogenih redoks reakcija na mjerene rezultate kada nam je od interesa isključivo heterogeni proces, a osobito u slučaju analize višekomponentnih sistema.

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