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The Effect of Slow Two-Electron Transfers and Disproportionation on Cyclic Voltammograms

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ABSTRACT

The EE mechanism (two-electron transfer) for cyclic voltammetry was investigated in considerable detail along with the effect of disproportionation. The theory was developed for either the first or second electron transfer being slow while the other one was reversible. It was possible to develop generalized working curves for the height and shape of the wave regardless of the difference in E° 's and the values of α and k_s . This theory was then applied to the analysis of the reduction of benzil in the presence of alkaline earth ions in dimethylformamide.

The theory for reversible and irreversible electron transfer has been examined in some detail previously for cyclic voltammetry (CV). The problem of multi-electron transfers in CV was studied first by Polcyn and Shain (1). The main quantitative emphasis was placed on the deconvolution of separated waves and only qualitative results were given for multi-electron waves. Myers and Shain (2) were able to quantitatively correlate the shape and peak current function of reversible voltammetric waves to their difference in E° 's if the E° 's were close together. It was found that the shape of the wave was independent of the relative values of the E° 's only if the difference in E° 's was greater than 180 mV. Otherwise, the wave will be broader than expected, even though it is still reversible. In addition, its shape and position are independent of scan rate. No correlations were made for quasi-reversible or irreversible electron transfers.

Multi-electron transfers can put a much more stringent demand on the rate of electron transfers if the wave is shifted significantly from its E° because of the second electron transfer. Ruzic (3) has shown that, for polarography, the apparent heterogeneous electron transfer rate constant, k_s' , for the over-all two-electron transfer is less than either of the individual rate constants, $k_{s,1}$ or $k_{s,2}$, if the second E° , E_2 , is more positive than the first E° , E_1 . In particular, the rate constant that is calculated using conventional theory is not the individual rate constant but an apparent one. Thus, the theory for quasireversible electron transfers in CV (4) yields the value of k_s' .

Competing with the multielectron transfer mechanism is the disproportionation mechanism. If the second electron transfer is so slow as to not be important and if E_2 is positive of E_1 , the classical disproportionation mechanism can then occur. The theory for this mechanism has been developed and verified by Saveant (5). But very little work has been done in trying to assess the relative importance of the electron transfer mechanism (EE) as compared to the disproportionation (DISP) mechanism. For reversible electron transfers the cyclic voltammograms will not distinguish between these two mechanisms.

It is the purpose of this work to develop the cyclic voltammetric theory more generally for the EE mechanism, including the possibility of disproportionation, and to verify it experimentally. The emphasis will be placed on those cases where only one wave is observed, and either the first or second electron transfer is slow. Recent studies have shown several reductions that are now known to follow the EE mechanism (6). In this study, the electrochemical reduction of benzil in dimethylformamide (DMF) in the presence of alkaline

earth salts, which is known to be a quasireversible two-electron transfer (6), is investigated in more detail in this work using the theory that is presented.

Experimental

Spectroquality N,N-dimethylformamide was obtained from Matheson, Coleman, and Bell. The solvents were dried as required using activated molecular sieves. Strontium and barium perchlorate were obtained from G. F. Smith Chemical Company and were vacuum dried at 250°C for 6 hr (7). Benzil was recrystallized from ethanol. The reference electrode is the same as was described in Ref. (6). Positive feedback resistance compensation was used in all of the fast scan rate experiments. A hanging mercury drop electrode was used as the working electrode. All solutions were de-aerated with dry nitrogen. The diffusion equations were solved numerically using the technique of digital simulation (8). The flux equations for a two-electron transfer that were derived by Feldberg (9) were used to calculate the current.

Theory

The generalized EE mechanism that is discussed in this paper is given by reactions [1]-[3]



Each electron transfer has associated with it a $k_{s,i}$ and α_i value, where $i = 1$ or 2 , for the first or second electron transfer, respectively. The analysis of the mechanism is divided into two major sections, depending upon whether the first or second electron transfer is rate limiting. In both cases, the mechanism is studied in the regions where only one wave is seen.

While each individual step has an α_i associated with it, the over-all electron transfer coefficient that is observed if one wave is seen has been derived by Mohilner (10). If the first electron transfer is limiting, then

$$\alpha n = \alpha_1 \quad [4]$$

If the second electron transfer step is limiting, the observed αn is

$$\alpha n = 1 + \alpha_2 \quad [5]$$

First-electron transfer limiting.—Reversible electron transfer.—Using the theory that was derived for polarography (3) and verified by digital simulation in this work for CV, the value of k_s' can be calculated as follows

$$k_s' = k_{s,1} \exp[-\alpha_1 F \Delta E / 2RT] \quad [6]$$

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Key words: EE mechanism, cyclic voltammetry, disproportionation.

where $\Delta E = E_2 - E_1$. As stated earlier, it is the k_s' value that is experimentally measured. Thus, α_1 and ΔE must be known in order to calculate $k_{s,1}$. In order to generalize the results, the dimensionless electron transfer rate parameter, ψ , will be used and is defined as follows

$$\psi = k_s / \sqrt{\pi a D_A} \quad [7]$$

and

$$a = nFv/RT \quad [8]$$

where v is the scan rate and the other terms have either been defined or have their usual electrochemical significance. Combining Eq. [6] and [7], we obtain

$$\psi_1' = \psi_1 \exp \left[\frac{-\alpha_1 F \Delta E}{2RT} \right] \quad [9]$$

The shape of the cyclic voltammogram depends on its reversibility (ψ_1') and on the difference in E^o 's (ΔE). These are two different parameters which must be evaluated separately. Cyclic voltammograms can be divided into three general classes depending on the value of ψ_1' . These classes are: (i) reversible, $\psi_1' > 7$, (ii) quasireversible, $0.1 < \psi_1' < 7$; and (iii) irreversible, $\psi_1' < 0.1$. Within these three classes, the shape of the wave is also dependent upon ΔE . In this paper, for each of the three classes, the effect of ΔE on these classes is examined. Several limiting cases have already been described. For the reversible and irreversible classes, Nicholson and Shain (11) have derived the shape and behavior of the wave if $\Delta E > 180$ mV. Myers and Shain (2) and Polcyn and Shain (1) have investigated the reversible case if $\Delta E < 180$ mV. These papers can be consulted to determine the shape of the wave and the value of ΔE . The irreversible case was also studied by Polcyn and Shain (1) for $\Delta E < 180$ mV but quantitative analysis was possible only if two waves were seen.

The disproportionation reaction (reaction [3]) has no effect on the shape of the wave if the first electron transfer is the slow step. This is because B is rapidly reduced to C at the electrode surface. This is not to say that the disproportionation reaction does not occur but only that the reaction has no effect on the wave when it occurs in this situation. This was verified by digital simulation.

Quasireversible electron transfer.—For quasireversible electron transfers, the shape of the wave depends upon ψ_1' and ΔE , and is not very dependent upon α_1 . If ΔE is larger than 180 mV, the value of k_s' can be calculated from the theory for quasireversible waves given by Nicholson (4). But even for $\Delta E > 180$ mV, noticeable deviations occur when the waves are simulated by the digital simulation technique (8, 9). The results are shown in Table I for ψ_1' less than 1. The deviations are due to the greater effect of α_1 on the peak potentials for the same value of ψ .

To calculate $k_{s,1}$, ΔE and α_1 must be known. The value of α_1 cannot be accurately determined unless scan rates large enough to make the wave irreversible are used. At these large scan rates, the theory presented in the next subsection on irreversible electron transfers can be used to calculate α_1 . The value of ΔE can be calculated using the reversible theory if slow enough scan rates can be achieved or by using the irreversible theory that is described for fast scan rates. For ΔE values less than 180 mV, the working curve

will depend upon ΔE in addition to ψ_1' . This effect is not large and can be corrected for in the same way as shown in Eq. [32] later in this paper.

Irreversible electron transfer.—In the case where single scan is used, the position, shape, and size of the reduction wave depends on the value of ψ_1' , α_1 , and ΔE . The wave does not occur at its thermodynamically defined E^o but at a more negative potential depending upon scan rate. In the theory as derived by Nicholson and Shain (11) for multielectron irreversible transfer, it was assumed that all the electron transfers except the slow one were fast, at least at the potentials where the reduction wave occurs. Polcyn and Shain (1) have shown that the wave will be affected if this assumption does not hold true but no quantitative theory was derived if one wave is observed. In order to provide a quantitative measure of the relative difference in reduction potentials, the parameter, ΔE_{AB} , is defined as

$$\Delta E_{AB} = \Delta E - \frac{59}{\alpha_1} \log \psi_1 \quad [10]$$

This equation is derived from the fact that an irreversible reduction is shifted to more negative potentials by a rate of $59/\alpha_1 \log \psi_1$. This parameter corrects ΔE for the fact that irreversible reductions do not occur at their thermodynamically defined potential but at some more negative potential depending upon α_1 and $k_{s,1}$. Similar to reversible electron transfer, only one wave is seen if ΔE_{AB} is positive and two waves are seen if ΔE_{AB} is negative enough. The exact values of these regions are shown later. By combining Eq. [9] and [10], ΔE_{AB} can be defined in terms of ψ_1' , which is experimentally measured

$$\Delta E_{AB} = \Delta E/2 - \frac{59}{\alpha_1} \log \psi_1' \quad [11]$$

By using digital simulation (8), it was found that the theory for irreversible electron transfers derived by Nicholson and Shain (11) can be used if ΔE_{AB} is greater than $75/\alpha_1$ mV. In this case, the following diagnostic criteria for the cathodic peak potential, E_{pc} , the cathodic peak current, i_{pc} , and the peak $E_{pp/2}$ values can be calculated

$$i_{pc} = 0.992 F A C_A^* \sqrt{\alpha_1 D_A a} \quad [12]$$

$$E_{pp/2} = E_{pc} - E_{p/2} = 47.7/\alpha_1 \text{ mV} \quad [13]$$

$$dE_{pc}/d \log v = 30/\alpha_1 \text{ mV} \quad [14]$$

and

$$\alpha_1 = Fv/RT \quad [15]$$

and where $E_{p/2}$ is the half-peak potential.

If ΔE_{AB} is less than $75/\alpha_1$ mV and only one wave is seen, the shape of the wave is changed from that predicted for an irreversible electron transfer and depends upon the scan rate. This is shown in Fig. 1 for three different values of ΔE_{AB} . As the scan rate is increased (ΔE_{AB} larger), the value of ΔE_{AB} will increase so as to make the wave approach the irreversible theory as given in Eq. [12]–[14]. The $E_{pp/2}$ value is most strongly dependent upon ΔE_{AB} for ΔE_{AB} values less than $75/\alpha_1$ mV. The variation of $E_{pp/2}$ values with ΔE_{AB} is shown in Fig. 2 for various values of α_1 , where the $E_{pp/2}$ values have been normalized in the following manner

$$E^*_{pp/2} = \alpha_1 E_{pp/2} \quad [16]$$

For large negative values of ΔE_{AB} two waves are seen and each wave can be analyzed individually because A will reduce prior to the potential for the B wave. For intermediate values of ΔE_{AB} , the A reduction wave will overlap the B wave and hence a broadened wave will be seen. There is a maximum value for which ΔE can have and still see the behavior as described in Fig. 2. For the wave to begin to broaden, ΔE_{AB} must be less than $75/\alpha_1$ mV and ψ_1' must be less than 0.1. Thus, rearranging Eq. [11], we obtain

Table I. Variation of ΔE_p values as a function of ψ_1' ($\alpha_1 = 0.5$)

ψ_1'	ΔE_p (mV)	
	EE mech-anism	Ref. (4)
1.0	45	42
0.5	61	53
0.2	107	79
0.1	156	106

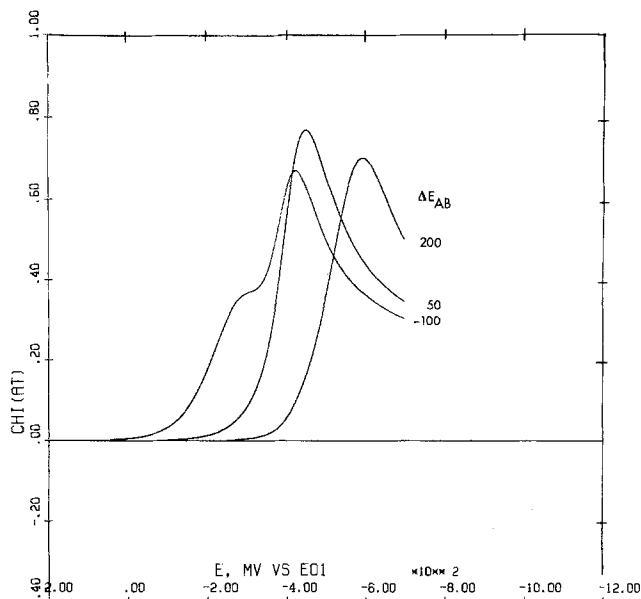


Fig. 1. The simulated cathodic scan for three different values of ΔE_{AB} (first-electron transfer irreversible).

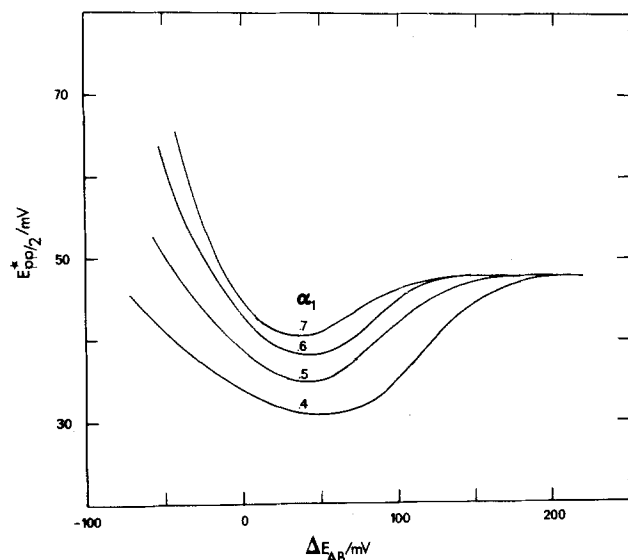


Fig. 2. The variation of $E_{pp/2}^*$ as a function of ΔE_{AB} for various values of α_1 in the case where the first electron transfer is irreversible.

$$\Delta E < \frac{32}{\alpha_1} \text{ mV} \quad [17]$$

Otherwise, Eq. [12]-[14] will always hold when the wave is irreversible. In the limit of very slow scan rates, the $E_{pp/2}$ value is limited by the value derived by Myers and Shain (2). The peak current function goes through a maximum at the same point that the $E_{pp/2}$ values go through a minimum but the change in this parameter is not very large with the maximum change on the order of 20%, making this parameter less useful.

In the cyclic experiment, on the anodic scan, the reverse of reactions [1] and [2] occurs



For the return peak, reaction [19] is rate limiting, which is the second-electron transfer. A full discussion of this case is given in the next section and only a few pertinent details are given here. Either one or two

waves can be seen on the return scan. The experimental conditions for the number of peaks that are seen are given in the next section.

With the information from the reverse scan, it is possible to determine all the parameters for the two-electron transfer. There are four unknowns which need to be evaluated from the experimental data. They are: E_1 , E_2 , $k_{s,1}$ and α_1 . There are two other parameters that are related to these and are calculated during the analysis. They are

$$E_{1,2} = (E_1 + E_2)/2 \quad [20]$$

and ΔE . It is the aim of the rest of this section to develop the equations necessary to calculate these parameters from the data.

If two anodic peaks are seen, E_2 can be found directly from the most negative peak potential, $E_{pa(2)}$, because that wave will occur at its thermodynamically defined potential

$$E_2 = E_{pa(2)} - 0.0285 \quad [21]$$

The value of α_1 can be determined from several methods depending on the value of ΔE_{AB} . If Eq. [12]-[14] are obeyed, α_1 can be determined from the shift in E_{pc} or by the $E_{pp/2}$ value. If ΔE_{AB} is less than $75/\alpha_1$ mV (in other words, the shape depends upon scan rate), the value of α_1 can be determined from the more positive anodic peak potential, $E_{pa(1)}$. Thus

$$\frac{dE_{pa(1)}}{d \log v} = \frac{30}{1 - \alpha_1} \text{ mV} \quad [22]$$

The cathodic peak potential can be related to the $E_{1,2}$ value by the following equation (11) if $\Delta E_{AB} > 75/\alpha_1$ mV

$$E_{pc} = E_{1,2} - \frac{RT}{\alpha_1 F} \left(0.339 - \log \psi_1' + \sqrt{\frac{\alpha_1}{2\pi}} \right) \quad [23]$$

and $E_{pa(1)}$ is

$$E_{pa} = E_{1,2} + \frac{RT}{(1 - \alpha_1)F} \left(0.339 - \log \psi_1' + \log \sqrt{\frac{1 - \alpha_1}{\pi}} \right) \quad [24]$$

By taking the difference in the peak potentials, we obtain

$$\Delta E_p = \frac{0.059}{\alpha_1(1 - \alpha_1)} (0.339 - \log \psi_1') + \frac{0.059}{1 - \alpha_1} \log \sqrt{\frac{1 - \alpha_1}{\pi}} + \frac{0.059}{\alpha_1} \log \sqrt{\frac{\alpha_1}{2\pi}} \quad [25]$$

Thus, since α_1 is known, ψ_1' can be calculated from the ΔE_p values. If ψ_1' is now substituted in Eq. [23], $E_{1,2}$ can be found. The value of E_2 is known from Eq. [21] so E_1 can be calculated by using Eq. [20].

If only one anodic peak is seen, α_1 can be found from the anodic or cathodic wave. If the anodic peak potential is used to calculate α_1 , then as will be described in the next section, Eq. [26] must be used

$$\frac{dE_{pa}}{d \log v} = 30/(2 - \alpha_1) \text{ mV} \quad [26]$$

The value of ψ_1' can be found, as before, from the ΔE_p value but Eq. [28] must be used because E_{pa} is given by

$$E_{pa} = E_{1,2} + \frac{0.059}{2 - \alpha_1} \left[0.339 + \log \psi_1' + \log \sqrt{\frac{1 - \alpha_1}{2\pi}} \right] \quad [27]$$

Using Eq. [27], the variation of ΔE_p with ψ_1' is given by

$$\Delta E_p = \frac{0.118}{\alpha_1(2 - \alpha_1)} (0.339 + \log \psi_1') + \frac{0.059}{2 - \alpha_1} \log \sqrt{\frac{1 - \alpha_1}{2\pi}} + \frac{0.059}{\alpha_1} \log \sqrt{\frac{\alpha_1}{2\pi}} \quad [28]$$

The value of $E_{1,2}$ can be found from Eq. [23]. The final problem is to find a method to determine E_1 and E_2 from $E_{1,2}$. To do this, either fast or slow scan rates must be used to separate either the anodic or cathodic peaks into two waves. It is theoretically possible to cause the cathodic peak to split apart if ΔE is less than -60 mV. If this is not possible, then scan rates fast enough to split the anodic peak apart must be used. If the cathodic peak begins to split apart, Fig. 2 can be used to calculate the value of ΔE_{AB} from the $E_{pp/2}$ values. From Eq. [11], it is possible to determine ΔE because α_1 and ψ_1' are known

$$\Delta E = 2 \left(\Delta E_{AB} + \frac{59}{\alpha_1} \log \psi_1' \right) \quad [29]$$

Unless there is some change in the shape of either the anodic or cathodic wave it is impossible to determine E_1 and E_2 .

Second-electron transfer limiting.—No disproportionation.—If the disproportionation reaction (reaction [3]) does not occur, the only way of producing C is by the direct reduction of B at the electrode surface. As with the previous case, an apparent electron transfer rate constant, k_s' , is observed experimentally rather than the actual k_s value of the second step. The value of k_s' is given by

$$k_s' = k_{s,2} \exp \left(- (1 - \alpha_2) \frac{F}{RT} \frac{\Delta E}{2} \right) \quad [30]$$

or

$$\psi_2' = \psi_2 \exp \left[- (1 - \alpha_2) \frac{F}{RT} \frac{\Delta E}{2} \right] \quad [31]$$

As before, reversible behavior is observed if ψ_2' is greater than 7. If ψ_2' is less than 0.1, an irreversible wave is seen. For reversible waves, the shape of the wave (2) depends only on ΔE and is independent of ΔE if ΔE is greater than 180 mV.

Quasireversible electron transfer.—For quasireversible waves, the shape of the wave depends upon ψ_2' and ΔE and is not very dependent upon α_2 . If ΔE is larger than 180 mV and ψ_2' greater than 0.5, the value of k_s' can be calculated from the theory for quasireversible waves given by Nicholson (4). The ΔE_p values as calculated by digital simulation for different α_2 values are given in Table II for several ψ_2' values less than 1.

If ΔE is less than 180 mV, the ΔE_p values are larger than predicted by Ref. (4). To a close approximation, the working curves for $\Delta E < 180$ mV can be obtained by adding the excess broadness, E_{exc} , as defined in Eq. [32] to the data in Table II

$$E_{exc} = \Delta E_{pr} - 29 \text{ mV} \quad [32]$$

where ΔE_{pr} is the ΔE_p value for a given ΔE (reversible case).

Irreversible case.—With a single scan, as defined earlier, the wave is irreversible if ψ_2' is less than 0.1.

Table II. Variation of ΔE_p values as a function of ψ_2'

ψ_2'	ΔE_p (mV)			Ref. (4)
	$\alpha_2 = 0.35$	0.5	0.65	
1.0	44	44	43	42
0.5	58	56	53	53
0.2	91	88	85	79
0.1	128	135	147	106

Irreversibility of the second electron transfer makes the second electron transfer occur at more negative potentials. In order to correct for this, we can define a parameter, ΔE_{BC} , which takes into account the effect of the slow electron transfer

$$\Delta E_{BC} = \Delta E/2 + \frac{59}{1 + \alpha_2} \log \psi_2' \quad [33]$$

This parameter normalizes the combined effects of ΔE and ψ_2' on the relative positions of the two waves. From digital simulation, it was found that, if ΔE_{BC} is greater than 50 mV, the shape of the wave is given by the theory derived by Nicholson and Shain (11). Substituting $n = 2$ and $\alpha n = 1 + \alpha_2$, the following diagnostic parameters can be calculated

$$i_p = 0.992 FA \sqrt{(1 + \alpha_2) D a_1 C_A^*} \quad [34]$$

$$E_{pp/2} = 47.7/(1 + \alpha_2) \text{ mV} \quad [35]$$

$$dE_p/d \log v = 30/(1 + \alpha_2) \text{ mV} \quad [36]$$

If ΔE_{BC} is less than 50 mV the wave will broaden and the peak current function will decrease. This effect can be seen in Fig. 3 for three different values of ΔE_{BC} . The variation in χ_p and $E_{pp/2}$ values can be calculated as a function of α_2 by the following normalizations

$$\chi_p^* = \chi_p/(1 + \alpha_2)^{1/2} \quad [37]$$

$$E_{pp/2}^* = E_{pp/2}(1 + \alpha_2) \quad [38]$$

The effect of ΔE_{BC} on χ_p^* and $E_{pp/2}^*$ is shown in Fig. 4 and 5. The variations in these parameters are qualitatively similar to the ECE and DISP mechanisms. It is only at fast scan rates that the χ_p and $E_{pp/2}$ values differ significantly from the ECE and DISP mechanism. But chronoamperometry will easily distinguish between these mechanisms because a two-electron diffusion-controlled wave can be obtained if a negative enough potential is used. In contrast, an ECE or DISP mechanism will show the slow kinetic step regardless of applied potential.

In a cyclic experiment, since the B to C reduction is limiting in this case, the C to B oxidation will be limiting on the reverse scan. Thus, the theory for the first-step limiting must be used to evaluate the oxidation peak.

As before, there are four parameters which must be determined: E_1 , E_2 , $k_{s,2}$, and α_2 . Thus, four indepen-

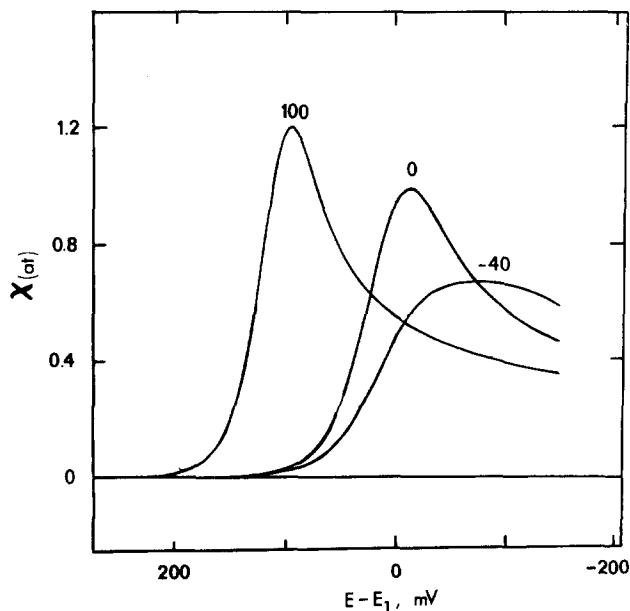


Fig. 3. The simulated cathodic scan for three different values of ΔE_{BC} (second-electron transfer irreversible).

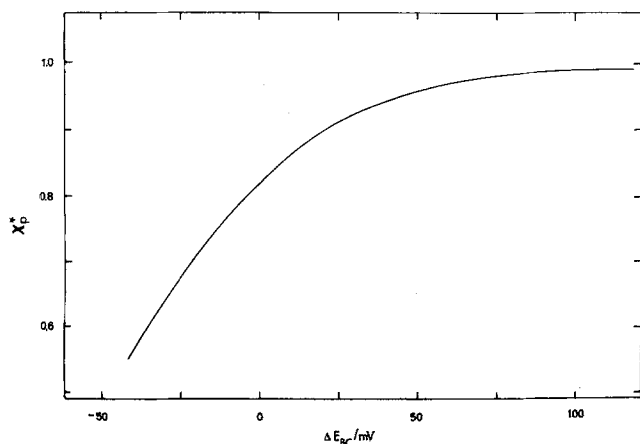


Fig. 4. The variation of χ_p^* as a function of ΔE_{BC} for the case where the second electron transfer is irreversible.

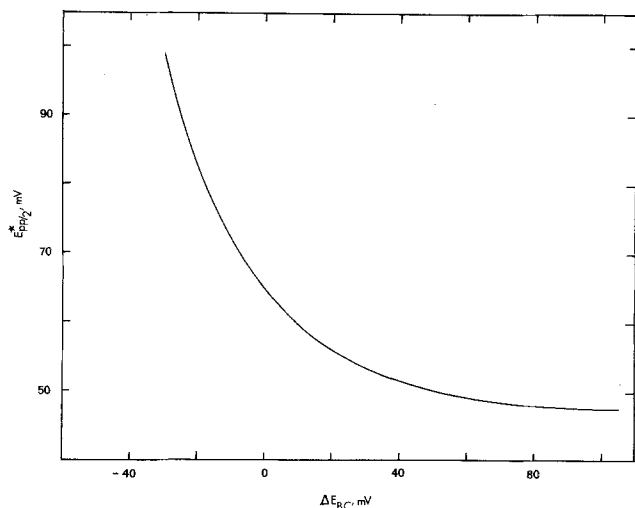


Fig. 5. The variation of $E_{pp/2}^*$ as a function of ΔE_{BC} for the case where the second electron transfer is irreversible.

dent equations must be derived. Only one anodic peak can be seen under practically any conditions where only one cathodic peak is seen as a consequence of Eq. [17]. This limits the existence of two peaks to ΔE values which are close to zero or negative. The value of α_2 can be calculated from Eq. [35] or [36]. The second equation that can be used to calculate these parameters is the cathodic peak potential (11), which is

$$E_{pc} = E_{1,2} - \frac{0.059}{1 + \alpha_2} \left[0.339 - \log \psi_2' + \log \sqrt{\frac{\alpha_2}{2\pi}} \right] \quad [39]$$

In addition, E_{pa} is given by (11)

$$E_{pa} = E_{1,2} + \frac{0.059}{1 - \alpha_2} \left[0.339 - \log \psi_2' + \log \sqrt{\frac{1 - \alpha_2}{2\pi}} \right] \quad [40]$$

Combining Eq. [39] and [40], the ΔE_p values can be derived as a function of ψ_2'

$$\Delta E_p = \frac{0.118}{1 - \alpha_2} (0.339 - \log \psi_2') + \frac{0.059}{1 + \alpha_2} \log \sqrt{\frac{\alpha_2}{2\pi}} + \frac{0.059}{1 - \alpha_2} \log \sqrt{\frac{1 - \alpha_2}{2\pi}} \quad [41]$$

Once ψ_2' is calculated, $E_{1,2}$ can be calculated from Eq. [39]. The final determination of E_1 or E_2 requires that ΔE_{BC} be less than 50 mV so that the wave will begin to split apart. If ΔE_{BC} can be determined from the $E_{pp/2}$ or χ_p values, then

$$\Delta E = 2 \left(\Delta E_{BC} - \frac{59}{1 + \alpha_2} \log \psi_2' \right) \quad [42]$$

If ΔE is such that the wave does not begin to split apart, then a lower limit on ΔE can be established because ΔE_{BC} must be greater than 50 mV

$$\Delta E > 100 - \frac{118}{1 + \alpha_2} \log \psi_2' \quad [43]$$

Thus, from Eq. [35] or [36], [39], and [41] and [42], we have four independent equations which allow one to calculate $k_{s,2}$, α_2 , E_1 and E_2 . The solution is simple because there is only one new unknown in each equation. It is important to obtain a good determination of α_2 since this is critical in all the equations. If the wave is beginning to split apart, it is probably more accurate to use the anodic peak potential to determine α_2 because that will not be affected. But fortunately, it turns out that unless the wave has broadened considerably, the calculation of α_2 from Eq. [36] is also not seriously affected even though Eq. [35] cannot be used.

Disproportionation.—For $\Delta E > 0$, the disproportionation reaction is favorable and can compete with the electron transfer if it is fast enough. In order to discuss this mechanism quantitatively, the rate constant, k_d , is normalized as follows

$$\lambda_d = k_d C_A^* / a \quad [44]$$

where λ_d is the disproportionation kinetic parameter. It is important to keep in mind that λ_d depends upon C_A^* while ψ_2 does not. Thus, it is possible to change λ_d without changing ψ_2 at the same time. In Fig. 6, the effect of the disproportionation reaction can be seen quite clearly. In this figure, the wave becomes dependent upon the disproportionation reaction and not on the second electron transfer. The same type of behavior is demonstrated in Fig. 7, where the electron transfer predominates if it is large enough in spite of a fairly significant rate for the disproportionation reaction. Qualitatively, the DISP mechanism is most important for negative values of ΔE_{BC} . If ΔE_{BC} is positive, the difference in the shape and height of the wave due to these two mechanisms is not large.

The effect of the disproportionation reaction on the EE mechanism was determined by the use of digital simulation (8). The results are shown in Fig. 8 and 9 for the χ_p and E_{pc} values for $\alpha_2 = 0.5$ as a function of ΔE_{BC} . It is assumed in this case that the wave is ir-

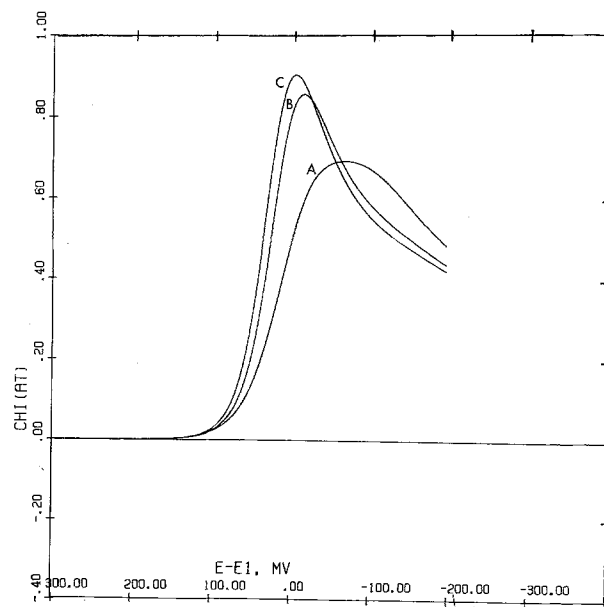


Fig. 6. The simulated cathodic scan for $\Delta E_{BC} = -20$ mV and (a) $\lambda_d = 0$; (b) $\lambda_d = 10$; and (c) $\lambda_d = 30$.

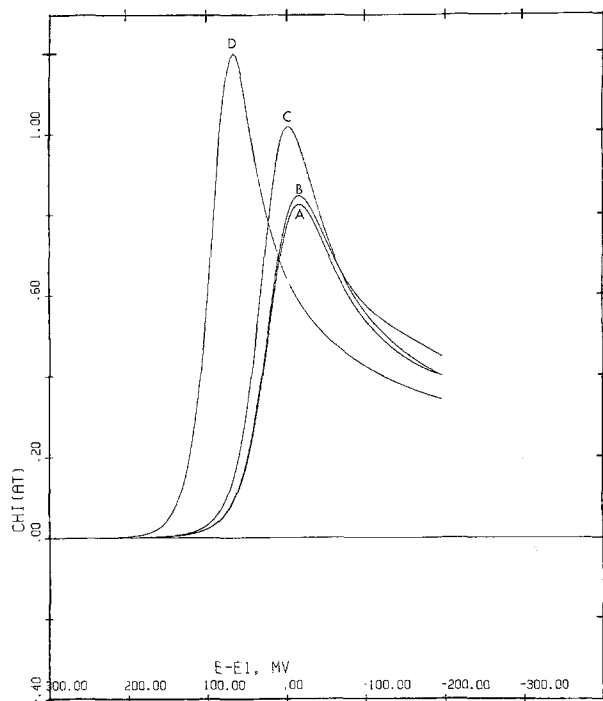


Fig. 7. The simulated cathodic scan for $\lambda_d = 10$, and ΔE_{BC} equal to (a) -100 mV; (b) -50 mV; (c) 0 ; (d) $+75$ mV.

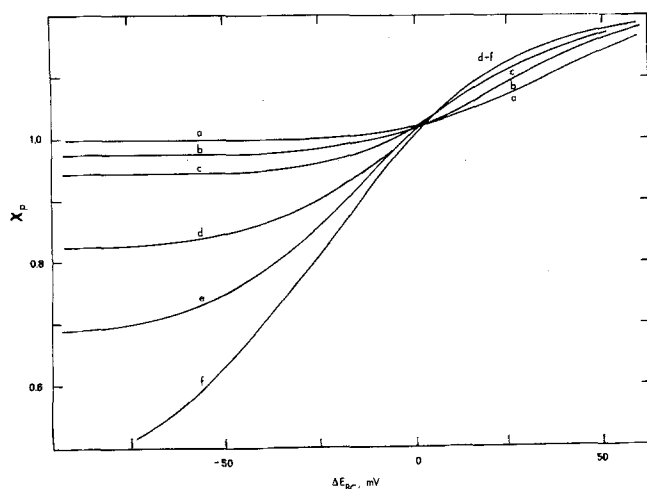


Fig. 8. The variation of χ_p as a function of ΔE_{BC} for various values of λ_d (second-electron transfer irreversible). (a) $\lambda_d = 1000$; (b) $\lambda_d = 300$; (c) $\lambda_d = 100$; (d) $\lambda_d = 30$; (e) $\lambda_d = 10$; (f) $\lambda_d = 0.1$.

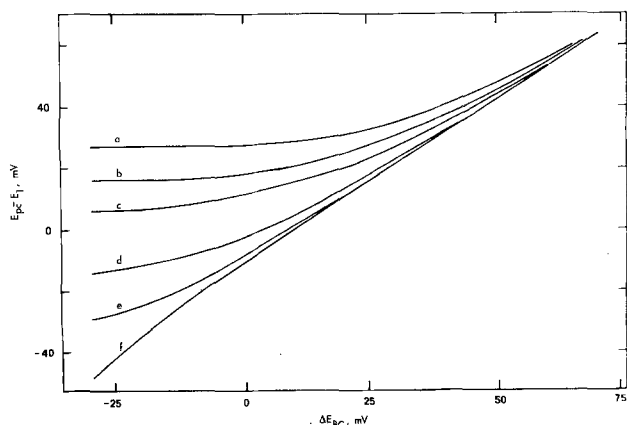


Fig. 9. The variation of $E_{pc} - E_1$ as a function of ΔE_{BC} for various values of λ_d . Values of λ_d given in Fig. 2.

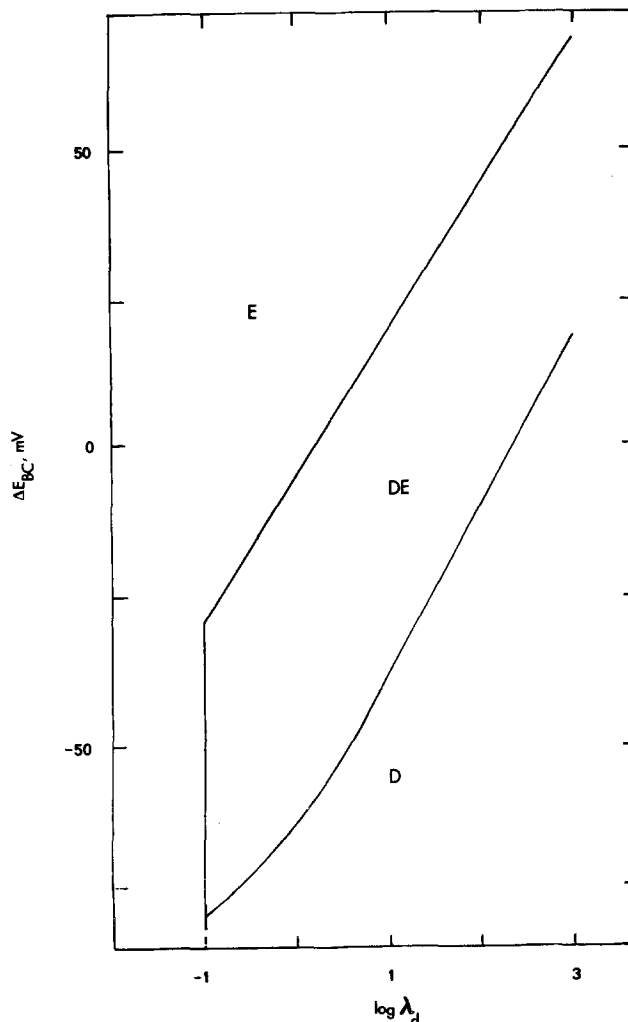


Fig. 10. Values of ΔE_{BC} and λ_d where various mechanisms are applicable. E = EE Mechanism, D = DISP Mechanism, DE = Mixture of EE, and DISP Mechanism.

reversible ($\psi_2' < 0.1$). For quasireversible and reversible waves, the effect of the DISP mechanism is small. Using the criteria that the DISP mechanism predominates if χ_p is within 5% of the value for the wave when $\psi_2' = 0$, a range of ΔE_{BC} values can be calculated and the results are shown in Fig. 10. At the other extreme, the wave is defined by the EE mechanism if the E_{pc} value is within 2 mV of the value obtained when $\lambda_d = 0$. These values are also shown in Fig. 10. Between these two limits, the wave is controlled by both the EE and DISP mechanism and Fig. 8 and 9 can be used. These limits can be expressed as follows

DISP mechanism predominates if

$$\Delta E_{BC} < 25 \log \lambda_d - 70 \text{ mV} \quad [45]$$

EE mechanism predominates if

$$\Delta E_{BC} > 25 \log \lambda_d - 5 \text{ mV} \quad [46]$$

While these results were obtained for $\alpha_2 = 0.5$, the same conclusions were obtained for $\alpha_2 = 0.35$ and 0.65 . The E_{pc} curve shown in Fig. 9 is almost independent of α_2 . The χ_p curve (Fig. 8) does depend upon α_2 because the limiting value of χ_p when ΔE_{BC} is large does depend upon α_2 . In general, this dependence is small and varies by only 10%, at most, for α_2 between 0.35 and 0.65 . But the limits given by Eq. [45] do not depend upon α_2 . This can be seen in Fig. 11 for $\alpha_2 = 0.35, 0.5$, and 0.65 and $\lambda_d = 10$.

Diagnostic Criteria and Data Analysis

The key to the analysis of cyclic voltammetric data for this case is a systematic approach. The analysis can

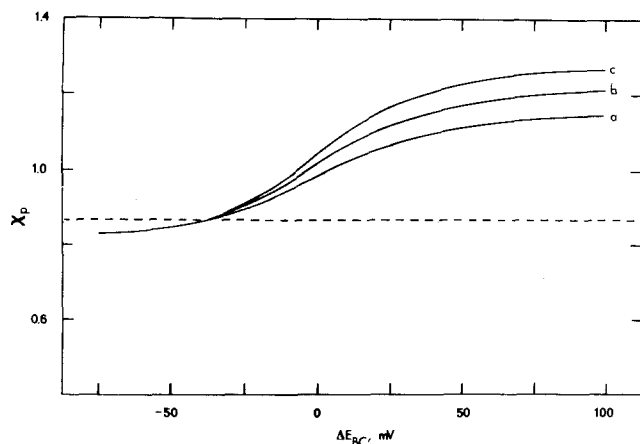


Fig. 11. Variation of χ_p as a function of ΔE_{BC} for $\lambda_d = 10$ and α_2 equal to (a) 0.35; (b) 0.50; and (c) 0.65. Dashed line indicates the value where χ_p has increased by 5%.

be segregated into the following steps:

1. determination that EE mechanism is occurring
2. determine if disproportionation is occurring
3. determination of the reversibility of electron transfer
4. identification of the slow step
5. calculation of electron transfer parameters

Step 1.—The determination that an EE mechanism is occurring is most easily done by double-potential step chronoamperometry. By comparison of the diffusion current with compounds of known electrochemical behavior, the n value can be calculated. Second, from the i_a/i_c ratio, the stability of the product can be verified and one can verify that no irreversible chemical reactions are occurring. Third, the $i_c \sqrt{t}/C_A^*$ value should be constant, indicating that no new electroactive products are formed. The value of the final potential must be negative enough so that the slow electron transfer step does not affect the $i_c \sqrt{t}/C_A^*$ value.

Step 2.—Since the value of λ_d depends upon C_A^* , the shape and position of the wave should be dependent upon C_A^* . Conversely, ψ' is independent of C_A^* , so one can determine if disproportionation is important under the conditions used.

Step 3.—If the shape or position of the wave is independent of scan rate, then the electron transfers are reversible. If the values of ΔE_p are between 30 and 150 mV, at least one of the electron transfers is slow and the wave is quasireversible. If the ΔE_p values are greater than 150 mV, the electron transfer is irreversible.

Step 4.—The identity of the slow step can be surmised from several ways depending upon the rate of the electron transfers. If the wave is quasireversible, it is difficult to determine the slow step because of the similarities in working curves. Only if scan rates large enough so that ψ' is < 0.1 , (i.e., the wave is irreversible) are used can one determine which step is slow.

If the electron transfer is irreversible, the identity of the slow step can be easily determined from the ratio of the peak currents, $i_{p,a}/i_{p,c}$, where $i_{p,a}$ is measured from a baseline calculated from the $t^{-1/2}$ decay of the cathodic current. If the first step is slow, then from Eq. [12] and [34]

$$i_{p,a}/i_{p,c} = \sqrt{(2 - \alpha_1)/\alpha_1} \quad [47]$$

Since $\alpha_1 < 1$

$$i_{p,a}/i_{p,c} > 1 \quad [48]$$

for all values of α_1 . Conversely, if the second electron transfer is slow

$$i_{p,a}/i_{p,c} = \sqrt{(1 - \alpha_2)/(1 + \alpha_2)} \quad [49]$$

Once again, α_2 is less than one. Thus

$$i_{p,a}/i_{p,c} < 1 \quad [50]$$

Substitution of typical values of α into Eq. [47] or [49] will show that there will be significant deviations from unity for the peak current ratio. In order to use this criterion with confidence, ψ' should be less than 0.1 ($\Delta E_p > 150$ mV) and reduced product must be stable.

Step 5.—The calculation of the parameters related to the electron transfer can now be determined once the previous steps have been completed. If the wave is reversible, only the $E_{1,2}$ value can be determined for sure. If ΔE is less than 180 mV, E_1 and E_2 can also be found. If the wave is quasireversible, then ψ' and $E_{1,2}$ can be calculated. Once again, if ΔE is less than 180 mV, E_1 and E_2 can also be found. If scan rates large enough to make the wave irreversible are used, α can be determined (and hence ψ if E_1 and E_2 are known). If the wave is irreversible, α can be calculated from the shape or shift in the wave and ψ' can be calculated from the ΔE_p values. Finally, $E_{1,2}$ can be found. If the values of ΔE_{AB} or ΔE_{BC} are appropriate, then E_1 , E_2 , and ψ can be found. In all this analysis, it is assumed that the other electron transfer remains reversible. This, in practice, limits the maximum scan rates which can be used to analyze the data by this method.

Results and Conclusions

The reduction of benzil (Bn) in 0.10F barium perchlorate with DMF as solvent is a two-electron quasireversible electron transfer. The cyclic voltammetric data for this solution is shown in Table III. Using the criteria discussed earlier, single and double step chronoamperometry verified that the reduction was a two-electron transfer for times at least as short as 1 msec and that the reduction product was stable. The second step in the analysis was to vary the concentration of benzil to determine if disproportionation was occurring. It was found that for C_{Bn} equal to 0.75 and 5.0 mM no change in the shape of the wave was observed (6). Thus, one could analyze the data in Table III without including the disproportionation reaction. The third step is to determine the reversibility of the electron transfer. Since ΔE_p is greater than 150 mV for all scan rates studied, the electron transfer is irreversible. Finally, because the $i_{p,a}/i_{p,c}$ ratios are much less than 1.0, the second electron transfer must be the slow step.

For the data below 1 V/sec, the experimental data fits quite well with the theory for an EE mechanism. From the ΔE_p values, it was possible to find α_2 , which is equal to 0.66. Equation [39], [41] and [42] can then be expressed in the following manner

$$\log \psi_2' = -4.78(\Delta E_p + 0.021) \quad [47]$$

$$E_{1,2} = E_{pc} + 0.0355(0.355 - \log \psi_2') \quad [48]$$

$$\Delta E = 2(\Delta E_{BC} - 0.0355 \log \psi_2') \quad [49]$$

The results obtained by these equations are shown in Table IV. Using these values as estimates, it was possible to generate theoretical voltammograms and compare them with the experimental data. This is shown in Fig. 12 for benzil at 100 mV/sec. The best values given in Table IV are obtained from the best fits of

Table III. Cyclic voltammetry of 0.75 mM benzil in DMF containing 0.10F Ba(ClO₄)₂

V (V/sec)	E_{pc}^*	ΔE_p (mV)	$E_{pp/2}$ (mV)
0.05	-1.419	156	39
0.1	-1.428	190	44
0.2	-1.438	221	48
0.5	-1.448	260	54
1.0	-1.457	285	58
5.0	-1.477	365	61
10.0	-1.500		63
20.0	-1.528		68

* V vs. SRE (silver reference electrode).

Table IV. Determination of second-electron transfer rate in 0.1F Ba(ClO₄)₂

V (V/sec)	ΔE_{BC} (mV)	ψ'	E_1^*	ΔE (mV)	K (M ⁻¹)	$k_{s,2}$ (cm/sec)
0.05	0	0.143	-1.407	60	1200	5.5×10^{-4}
0.1	-12	0.0983	-1.404	48	1350	5.0×10^{-4}
0.2	-18	0.0699	-1.412	46	1000	4.9×10^{-4}
0.5	-26	0.0455	-1.410	43	1060	5.0×10^{-4}
Best value			-1.408	55	1150	5.0×10^{-4}
Ref. (6)			-1.415	100	880	5×10^{-4}

* V vs. SRE.

the experimental data with the simulated voltammograms.

There occur significant deviations at scan rates above 1V/sec due to the slow rate of the first electron transfer. The values of $k_{s,1}$ and α_1 were determined by digital simulation, using the values already calculated for the second electron transfer. It was found that α_1 was equal to 0.7, and $k_{s,1}$ was equal to 6.5×10^{-3} cm/sec. The experimental data along with the theoretical curves are shown in Fig. 13 for the $E_{pp/2}$ values. An experimental voltammogram with the simulated wave is shown in Fig. 14 for benzil at 1.0 V/sec.

The rate of the first electron transfer appears to be unusually slow when compared to the rate of reduction with tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte. But once again we are dealing with an apparent electron transfer rate constant, $k_{s,1}^*$,

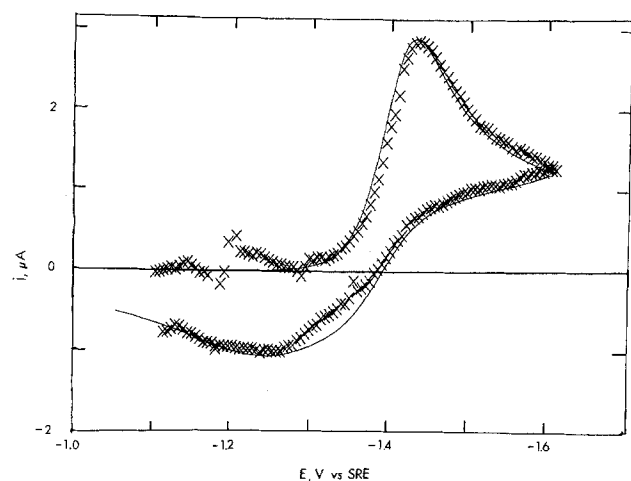


Fig. 12. Cyclic voltammogram for the reduction of 0.75 mM benzil in DMF with 0.10F Ba(ClO₄)₂. Scan rate = 100 mV/sec; solid line, theoretical; x, experimental points.

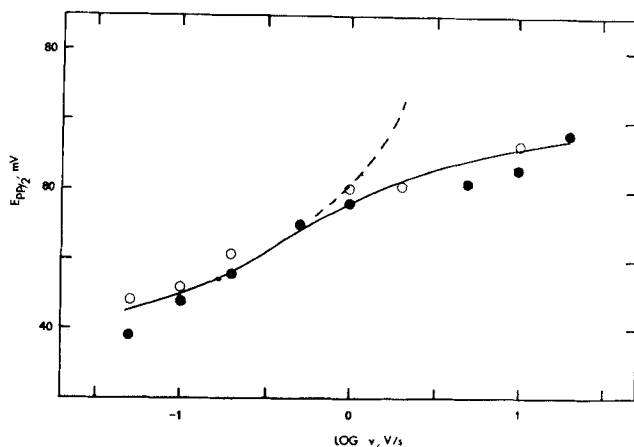


Fig. 13. The variation of $E_{pp/2}$ as a function of scan rate. Solid line, $k_{s,1} = 0.10$ cm/sec, $\alpha_1 = 0.7$, $k_{s,2} = 5.0 \times 10^{-4}$ cm/sec, $\alpha_2 = 0.66$; dashed line, first-electron transfer reversible; closed circles, $C_{Bn} = 0.75$ mM; open circles, $C_{Bn} = 5.0$ mM.

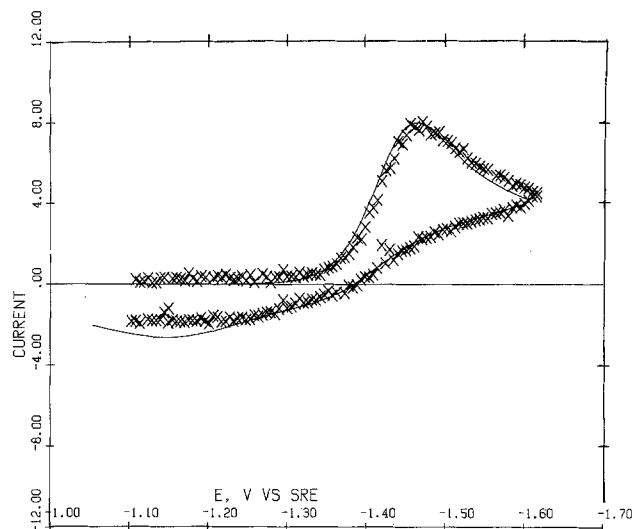
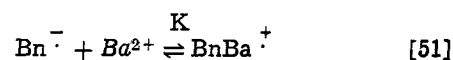
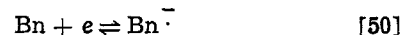


Fig. 14. Cyclic voltammogram for the reduction of 0.75 mM benzil in DMF with 0.10F Ba(ClO₄)₂. Scan rate = 1 V/sec; solid line, theoretical; x, experimental points.

instead of the true $k_{s,1}$. This is caused by the shift of the benzil



reduction from its equilibrium position being due to the ion-pairing reaction. Since the wave occurs positive of the potential where benzil alone is reduced, the heterogeneous forward rate constant, k_{hf} , at the peak potential is less than $k_{s,1}$ due to the exponential relationship between k_{hf} and $k_{s,1}$

$$k_{hf} = k_{s,1} \exp \left[-\alpha_1 \frac{nF}{RT} (E - E^0) \right] \quad [52]$$

If one solves the boundary value problem for the above reaction, it turns out that $k_{s,1}^*$ is related to $k_{s,1}$ by the following equation

$$k_{s,1}^* = k_{s,1} (1 + KC_{Ba})^{\alpha_1} \quad [53]$$

where C_{Ba} is the concentration of the barium ion. For $KC_{Ba} = 115$ and $\alpha_1 = 0.7$, $k_{s,1}$ is 0.18 cm/sec. This value of $k_{s,1}$ is within the range that has been observed for several quinones recently (12). This value is still smaller than the minimum value estimated in the presence of TBAP only. This difference cannot be due to ion pairing between the barium and perchlorate ions. While this will reduce $[Ba^{2+}]$, it will at the same time increase the value of K because the $K[Ba^{2+}]$ value was observed experimentally. In addition, estimations of the Ba-ClO₄ ion pair constant from Bjerrum's theory (13) and from data for Mg-ClO₄ in acetonitrile and acetone (14) indicate that ion pairing of the barium perchlorate electrolyte is insignificant in DMF. This lower rate constant could be due, though, to double layer changes caused by the presence of barium ions.

Using the information in Table IV, it is possible to estimate the maximum value for the disproportionation rate constant, k_d , using Eq. [45]. The maximum value of k_d depends upon scan rate, with the disproportionation reaction being more important at faster scan rates because ΔE_{BC} is decreasing. For $C_{Bn} = 0.75$ mM, it was found that k_d must be less than 700 M⁻¹ sec⁻¹. This maximum value may be too small to see. A more practical value is probably 3×10^3 M⁻¹ sec⁻¹. Since no disproportionation reaction is seen for the 5 mM solution, k_d must be less than 750 M⁻¹ sec⁻¹. It is interesting to note that if ψ_2' were zero, a value of $k_d = 750$ M⁻¹ sec⁻¹ could be easily seen and calculated. Thus, for $C_{Bn} = 5$ mM and $v = 50$ mV/sec; λ_d

would be 2.7. But this reaction, if it occurs, is obscured by the second electron transfer.

The determination of $k_{s,2}$ for the reduction of benzil in the presence of strontium ion can be accomplished in the same way. The α_2 value was again found to be 0.65. Thus, Eq. [47]-[49] could be used. The results are shown in Table V. The calculated values for the benzil reduction with the strontium ion present agree well with the values determined by trial-and-error simulation. As was seen before (6), the second-electron transfer is somewhat slower with the strontium ion pair than with the barium ion pair. This difference, though, could be due to double layer effects.

The simplicity of this method of analysis is quite evident. Previously, it was necessary to perform a considerable number of trial and error simulations before the best fit could be obtained in order to determine the electron transfer parameters for the EE mechanism. But by use of the equations given in the paper, it was possible to directly calculate the parameters. A second advantage is that it is possible to identify significant deviations from the EE mechanism, as was shown in this case for scan rates in excess of 1 V/sec with barium ions present. If an EE mechanism is occurring with only one of the k_s values being slow, the shape of the wave should follow the criteria given previously. In particular, a good diagnostic criteria is the shift in the anodic and cathodic peak potentials with scan rates. Consistent α values should be obtained from these calculations. A factor complicating the analysis is the situation where both electron transfers may be slow. The diagnostic criteria will obey qualitatively the analysis given in this paper, but will fail seriously upon quantitative analysis. Work is in prog-

Table V. Cyclic voltammetry of benzil in DMF containing 0.10F Sr(ClO₄)₂

V (V/sec)	$E_{pp/2}$ (mV)	ΔE_p (mV)	E_1^*	ΔE (mV)	$k_{s,2}$ (cm/sec)	K (M ⁻¹)
0.05	47	285	-1.372	72	1.4×10^{-4}	4800
0.1	49	322	-1.370	76	1.4×10^{-4}	5140
0.5	58	350	-1.383	80	1.7×10^{-4}	3100
Best value			-1.375	80	1.6×10^{-4}	4300
Ref. (6)			-1.397	135	2.0×10^{-4}	1800

* V vs. SRE.

ress in this laboratory to present similar methods for the analysis of this case.

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