Effect of Comproportionation on Voltammograms for Two-Electron Reactions with an Irreversible Second Electron Transfer

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Many organic and organometallic compounds are reduced or oxidized in two steps with the addition or removal of the second electron occurring with greater difficulty than the first. In such EE reactions, a comproportionation reaction can occur in solution near the electrode by which the final product exchanges an electron with the reactant to form two molecules of the intermediate species. Normally, this comproportionation reaction has little or no effect in voltammetry. In this paper, a substantial effect of comproportionation is predicted for the case where the second electron-transfer reaction is irreversible. In steadystate voltammetry, the normally symmetric, sigmoidshaped second wave is predicted to rise more sharply near its base than is observed in the absence of comproportionation and, in the limit of a very fast comproportionation reaction, an "onset potential" develops at which the current at the second wave increases abruptly from the limiting current of the first plateau. Experimental examples of these effects are presented for the reduction of tetracyanoquinodimethane in acetonitrile by steady-state microelectrode voltammetry, normal-pulse voltammetry, and cyclic voltammetry.

The consecutive addition or removal of two or more electrons is a commonly observed phenomenon in organic and organometallic electrochemistry. In systems featuring two electron-transfer reactions (EE systems), the individual formal potentials, $E^{\circ'_1}$ and $E^{\circ'_2}$, are normally separated by several tenths of a volt such that addition or removal of the second electron is more difficult than the first (reactions 1 and 2). For the sake of simplicity, the

$$A + e^- = A^{\bullet -} \qquad E^{\circ'}_{1}, k_{s,1}, \alpha_1$$
 (1)

$$A^{\bullet-} + e^- = A^{2-} \qquad E^{\circ'}{}_2, k_{s,2}, \alpha_2$$
 (2)

reactions are written as reductions and the initial reactant is neutral. Transposition to oxidation reactions and other reactant charge types is easily achieved. Each reaction is characterized by a formal potential (E°) , standard heterogeneous electron-transfer rate constant (k_s) , and transfer coefficient (α) .

For the case where introduction of the second electron occurs with greater difficulty than the first, it has long been recognized that the comproportionation reaction (reaction 3) is favored so that, at potentials where A^{2-} is being formed at the electrode,

$$A^{2-} + A = 2A^{-}$$
 (3)

incoming A will react with electrogenerated A^{2-} in the diffusion layer to form the intermediate radical anion, $A^{\bullet-}$. Normally, the effect of this comproportionation reaction on the voltammetric response is negligible. In fact, it was shown many years ago that comproportionation can have absolutely no effect in voltammetry for the case of mass transport by diffusion only, equal diffusion coefficients for all three species, reversible electrode reactions, and the absence of other chemical reactions involving the three species in the EE system.¹

When one or more of these conditions is not met, the comproportionation reaction will exert an effect on the voltammetric response. When diffusion is the only means of mass transport, the largest effects are seen when other chemical reactions are involved, e.g., conformational changes or isomerization reactions.^{2,3} The effect of unequal diffusion coefficients was explored recently,⁴ and it was found that small but detectable effects could be seen in normal-pulse voltammograms for oxidation of the dianion of tetracyanoquinodimethane, TCNQ²⁻, where the diffusion coefficient of the reactant is about 35% smaller than that of the intermediate (TCNQ^{*-}) or the final product (TCNQ). It is unusual for the diffusion coefficients of the structurally related species in an EE system to differ as much as was seen for TCNQ, so one expects that the effects of unequal diffusion coefficients will normally be scarcely noticeable.

Much more dramatic effects are seen when migration contributes to mass transport in the voltammetric experiment.^{5–9} This occurs when little or no supporting electrolyte is present. In steady-state experiments (microelectrode voltammetry, for ex-

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ample) the ratio of the two limiting currents can deviate markedly from the value of unity that is seen at high supporting electrolyte concentrations. Thorough theoretical treatments of migrational effects in EE systems have been published.8,9

In a recent study,¹⁰ we determined the infinite-dilution standard potentials, E°_{1} and E°_{2} , for TCNQ (referred to the infinite-dilution standard potential for the ferrocene/ferrocenium couple) by using steady-state microelectrode voltammetry at low ionic strength in well-supported solutions (ratio of electrolyte to TCNQ concentration equal to 10). In the course of these studies, we noted an unusual asymmetry in the shape of the second steady-state voltammetric wave under certain experimental conditions. Instead of exhibiting the normal-symmetric sigmoid shape, the second TCNQ wave featured a rather sharply rising current near its foot and a more normal drawn-out approach to the limiting current at the crest. We then noted that similar unusually shaped curves were present in our published normal-pulse voltammograms of TCNQ⁴ and in channel-flow voltammograms of 2,3-dichloro-5,6dicyano-1,4-benzoquinone.¹¹ In the present work, we have developed a probable explanation for these unusual wave shapes in terms of the effect of the comproportionation reaction when the second electron transfer exhibits sluggish electron-transfer kinetics.

EXPERIMENTAL SECTION

Solvent, electrolyte, and reagents were as described earlier.⁴ Standard procedures were employed for microelectrode voltammetry, rotating disk electrode voltammetry, and cyclic voltammetry. The reference electrode comprised a silver wire in contact with 0.010 M AgNO₃, 0.10 M Bu₄NPF₆ in acetonitrile (AgRE).

Simulations were carried out using the software package DigiSim (Bioanalytical Systems; Version 3.0). Hemispherical diffusion geometry was employed for simulations of microelectrode voltammetry. The expanding space factor was 0.2, $r_{0,\min}$ was 50, and the scan rate was 0.1 mV/s. These input parameters were found to produce very accurate values of the steady-state limiting current. Simulation of the normal-pulse voltammogram was accomplished using a mass transport coefficient for hemispherical diffusion (D/r_0) set equal to the experimental mass transport coefficient for normal-pulse voltammetry $((D/\pi t_p)^{1/2})$. Here *D* is the diffusion coefficient of the reactant, r_0 is the radius of the hemisphere, and t_p is the pulse duration. The simulated currents were scaled to match the experimental values.

RESULTS AND DISCUSSION

The concepts will be introduced by way of theoretical steadystate microelectrode voltammograms. Figure 1 includes simulations for an EE reaction occurring at a hemispherical microelectrode for the case where the first electron transfer occurs reversibly and the second is quite irreversible, $k_{s,2} = 10^{-4}$ cm/s. The inputs to the model and the simulation output have been expressed in real laboratory units rather than as dimensionless quantities. The intention is to facilitate perception of the relevance of the calculations to realistic laboratory conditions. Of course, the simulation results can be easily expressed in dimensionless



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Figure 1. Simulated steady-state voltammograms. $E^{\circ}_{1} = 0$ V, $k_{s,1}$ = 10⁴ cm/s, $\alpha_1 = 0.5$, $E^{\circ}_2 = -0.5$ V, $k_{s,1} = 10^{-4}$ cm/s, $\alpha_2 = 0.5$, D (all species) = 10^{-5} cm²/s, $C^*_{reactant} = 10^{-3}$ M, $r_0 = 10 \mu$ m, and k_{comp} as indicated; temperature was 298 K. Dashed curve: Limiting behavior for infinite k_{comp} with identification of the onset potential, E_{os} .

form if a generally applicable set of theoretical responses is needed. The values of input parameters are given in the caption to Figure 1.

The first wave is of reversible shape with $E_{1/2,1} = E_1^{\circ}$ and with the slope of the "log plot" (*E* vs $\log[(I_{\lim,1} - I)/I])$ equal to the reversible limit of 2.303RT/F (59.16 mV at 298 K).¹² Because of the small value of $k_{s,2}$ that was chosen, the second wave (with comproportionation suppressed; $k_{comp} = 0$) exhibits the normal sigmoid shape for an irreversible process, the slope of the log plot being $2.303RT/\alpha_2 F$ (118 mV for 298 K and $\alpha_2 = 0.5$, as chosen for the simulation).¹² The second half-wave potential, $E_{1/2,2}$, is displaced¹² (*RT*/ $\alpha_2 F$) ln($k_{s,2}r_0/D$) to negative potentials from E°_2 (236 mV for the values of parameters used in Figure 1). Thus, in the absence of comproportionation, the voltammogram is perfectly normal with the shape and position of the waves in accord with theory. These results support the conclusion that the simulation program is producing reliable results.

However, as comproportionation is introduced into the simulation by increasing k_{comp} , a dramatic change in the shape of the second wave is predicted. The wave tends to shift toward negative potentials and a marked asymmetry sets in at k_{comp} near 10⁸ M⁻¹ s⁻¹. The current rises very sharply at the foot of the wave while the shape near the limiting current is almost normal. In the limit of very large $k_{\rm comp}$, the current-potential curve near the foot is predicted to feature a sharp break (very large d^2I/dE^2). This "onset potential", E_{os} , is indicated in Figure 1.

It is of interest to see if we can understand the underlying causes of the development of the onset potential. At first glance, it is not obvious why a fast comproportionation will cause the effects that are seen. It is particularly curious that the comproportionation reaction somehow works to keep the currents in the range of about -0.6 to -0.7 V at the level of the first limiting current although, in the absence of comproportionation, this potential region encompasses a large part of the second wave. Clearly, the rate of electrode reaction 2 (A^{•-} + e \rightarrow A²⁻) is sufficiently high in this region to produce the second wave that is seen in the absence of comproportionation. The answer to this

⁽¹²⁾ Oldham, K. B.; Zoski, C. G. J. Electroanal. Chem. Interfacial Electrochem. 1988. 256. 11.

apparent contradiction is that the current produced by reaction 2 results in an equal suppression of the current arising from the steady-state arrival of A and its reduction by reaction 1 because the product of reaction 2, A^{2-} , destroys an equivalent amount of A when comproportionation is fast, i.e., $A^{2-} + A \rightarrow 2A^{-}$.

For the case of equal diffusion coefficients, the surface concentration of A^{•-}, $C_{A^{*-},x=0}$, will equal the bulk concentration of A, C^*_{A} , at any point on the first limiting current plateau. The rate of irreversible reaction 2 (expressed as the flux of A^{2-} produced, $J_{A^2,x=0}$) will be given by eq 4, which invokes the normal Butler– Volmer expression for the rate constant, $k_{f,2}$. Also, the flux of A at

$$J_{A^{2},x=0} = k_{f,2}C_{A^{\star-},x=0} = C^{*}{}_{A}k_{s,2} \exp\left[-\frac{\alpha_{2}F}{RT}(E-E^{\circ}{}_{2})\right]$$
(4)

the electrode surface when the steady-state current is equal to the first limiting current is given by eq $5.^{13}$ As long as the

$$J_{A,x=0} = -\frac{DC^{*}{}_{A}}{r_{0}}$$
(5)

magnitude of the flux of A^{2-} produced (eq 4) is less than the potential flux of A that can arrive at the surface (eq 5), the additional current due to production of A^{2-} will be exactly offset by suppression of the flux of arriving A by the fast comproportionation reaction that converts A^{2-} and A to two radical anions.

Following this line of argument, the onset potential, E_{os} , will occur at the point where the flux of A²⁻ produced (eq 4) first exceeds the maximum flux of A arriving at the surface. By equating the fluxes from eqs 4 and 5, we obtain an expression for the onset potential, eq 6. Interestingly, this expression for E_{os}

$$E_{\rm os} - E_2^{\circ} = \frac{RT}{\alpha_2 F} \ln\left(\frac{r_0 k_{\rm s,2}}{D}\right) \tag{6}$$

in the limit of a very fast comproportionation reaction is the same as the expression for $E_{1/2,2}$ in the absence of comproportionation.¹² For the parameter values used in Figure 1, E_{os} is predicted to be -236 mV from eq 6, and this is exactly what was found by simulation, an observation that again supports the conclusion that the simulation program is producing reliable results.

Another interesting feature of the second wave in the limit of very large $k_{\rm comp}$ (dashed curve, Figure 1) is that its location and shape are identical to those of the upper half of an irreversible wave with a limiting current equal to $I_{\rm lim,2}$. As was noted above, the half-wave potential of this hypothetical expanded wave falls at $E_{\rm os}$, which is identical to $E_{1/2,2}$ in the absence of comproportionation. Furthermore, the slope of the log plot of the upper half of the expanded wave (*E* vs log[$(I_{\rm lim,2} - I)/I$] is exactly 2.303*RT*/ $\alpha_2 F$. This result is mentioned here because it is interesting and, to the authors, quite unintuitive.

The geometry of the electrode does not play an explicit role in the development of eq 6. Thus, for the technique of normalpulse voltammetry at planar electrodes for the EE system being considered, an analogous treatment gives eq 7 for E_{os} where t_p is

$$E_{\rm os} - E_2^{\circ} = \frac{RT}{2\alpha_2 F} \ln\left(\frac{t_{\rm p} k_{\rm s,2}}{D}\right) \tag{7}$$

the pulse duration. In fact, it was in the context of normal-pulse voltammetry that unusually shaped voltammograms were first noticed for an EE mechanism.⁴ Analogous expressions can easily be derived for other steady-state (e.g., rotating disk voltammetry) or pseudo-steady-state (classical polarography) techniques. To our knowledge, the only earlier reference to phenomena like those discussed here is in the theoretical work of Ruzic and Smith on polarography and ac polarography.¹⁴

It is likely that similar effects on the second wave in EE processes with an irreversible second step are possible for all voltammetric techniques. In the present work, for example, we have demonstrated that onset potentials can be seen in cyclic voltammetry (see below). A substantially different but related effect has been observed for the reduction of cyclooctatetraene, for which the first electron-transfer reaction is quasireversible while the second is reversible.¹⁵

Returning to microelectrode voltammetry at hemispherical electrodes, it is of interest to determine how large the parameter $r_0 k_{s,2}/D$ can be before eq 6 begins to fail. Simulations were conducted for values of $r_0 k_{s,2}/D$ ranging from 10^{-8} to 10. From 10^{-8} to 1, the simulations gave values of E_{0s} in agreement (±1) mV) with eq 6, again attesting to the accuracy of the simulation program. Only when this kinetic parameter exceeded 1 did the simulations indicate a loss of definition of the onset potential under conditions where the comproportionation reaction is very fast. This information allows us to assess the likelihood that the unusually shaped waves we have been discussing will actually be seen under normal conditions and with typical EE systems. It is reasonable to doubt that sharp onset potentials will be seen because it is required that the comproportionation reaction be extremely fast while the kinetic parameter $r_0 k_{s,2}/D$ cannot be too large. A fast comproportionation reaction implies a low barrier for this solutionphase electron-transfer reaction which can result from a low intrinsic barrier and/or a large driving force. However, a low intrinsic barrier will require that the barrier for the heterogeneous electron transfer in reaction 2 will also be small, meaning that $k_{s,2}$ will be large.

Taking unity as the upper limit of $r_0k_{s,2}/D$ for observing a welldefined onset potential and using 10 μ m as a very convenient radius for a microelectrode along with a typical value of 10^{-5} cm²/s for the diffusion coefficient, we obtain the result that $k_{s,2}$ cannot exceed 0.01 cm/s to allow well-defined E_{os} . This rate constant is smaller than is typically observed for the electron-transfer reactions of organic and organometallic species that might take part in an EE scheme and may explain why sharp E_{os} values have not been seen.

In Figure 2, a normal-pulse voltammogram for the reduction of TCNQ at a platinum working electrode in acetonitrile with 0.10 M Bu_4NPF_6 is presented⁴ (circles). Also shown in Figure 2 are

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⁽¹⁴⁾ Ruzic, I.; Smith, D. E. J. Electroanal. Chem. Interfacial Electrochem. 1975, 58, 145.

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Figure 2. Normal-pulse voltammogram for reduction of 6.9×10^{-4} M tetracyanoquinodimethane (TCNQ) in acetonitrile with 0.10 M Bu₄-NPF₆ at 293 K (platinum disk working electrode (diameter: 0.31 cm)). Pulse duration: 0.050 s. Data (circles) were taken from ref 4. Lines are simulations with the following input parameters: $E^{\circ}_1 = -0.107$ V, $k_{s,1} = 10^4$ cm/s, $\alpha_1 = 0.5$, $E^{\circ}_2 = -0.658$ V, $k_{s,1} = 0.0065$ cm/s, $\alpha_2 = 0.35$; diffusion coefficients of neutral, radical anion, and dianion are 1.44×10^{-5} , 1.35×10^{-5} , and 9.1×10^{-6} cm²/s, respectively;⁴ k_{comp} as indicated.

simulations in which $E_1^{\circ} - E_2^{\circ}$ has been set at 0.55 V, in agreement with our earlier measurements for this ionic strength.¹⁰ With fast comproportionation ($k_{comp} = 10^8 \text{ M}^{-1} \text{ s}^{-1}$) and a rather small second electron-transfer rate constant ($k_{s,2} = 0.0065 \text{ cm/s}$), the second wave is positioned properly on the potential axis and its asymmetric shape agrees well with experiment. To generate a clear onset potential, the comproportionation reaction must approach the diffusion-controlled limit, ca. $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ (Figure 2). In the absence of comproportionation ($k_{comp} = 0$, Figure 2), the second wave has a symmetric shape and its half-wave potential is about 60 mV less negative than when the comporoportionation reaction is fast. Though $k_{comp} = 10^8 \text{ M}^{-1} \text{ s}^{-1}$ provides the best agreement with the experimental data, the response is quite insensitive to k_{comp} when it is large so this is not a practical way to evaluate k_{comp} accurately.

We speculate that the rather small value of $k_{s,2}$ required to match the experimental data may have resulted from deactivation of the electrode due to adsorption of impurities, electrolysis products, etc. Some asymmetry is seen in the second wave of steady-state voltammograms obtained with platinum microelectrodes ($r_0 = 5 \mu$ m), but it is not as marked as the result in Figure 2. Freshly polished electrodes tend to give more symmetric responses, implying that they exhibit larger values of $k_{s,2}$. When studied at a rotating platinum disk electrode (RDE), the second wave for reduction of TCNQ was quite symmetric up to our maximum rotation rate of 2000 rpm. In general, enhanced mass transport should put stress on the second electron-transfer reaction (reaction 2), bringing about a breakdown in symmetry or even the development of a sharp break in the voltammogram.



Figure 3. Cyclic voltammogram of 1.30 mM TCNQ in acetonitrile with 0.10 M Bu_4NPF_6 at 298 K (platinum disk working electrode (diameter: 0.33 cm). Scan rate: 2.00 V/s.

Apparently, larger rotation rates are required to cause such behavior for TCNQ and the RDE.

Analogous behavior is easily seen in cyclic voltammetry. Figure 3 shows a voltammogram obtained at 2 V/s in which a rather sharp break is observed at the foot of the second cathodic peak. Similar shapes were observed for concentrations ranging from 0.2 to 3 mM and scan rates from 1 to 50 V/s. The voltammograms are well accounted for by digital simulations that include fast comproportionation though the agreement is not perfect, suggesting that other factors are influencing the shape. If the comproportionation reaction is eliminated from the simulations, even qualitative agreement with the shape of the experimental voltammograms is impossible to achieve.

As stated in the introduction, comproportionation will not affect voltammograms if the diffusion coefficients of all species are equal, mass transport is by diffusion only, the electron-transfer reactions are reversible, and none of the species take part in other chemical reactions. In this work, we have reported an experimental example of the effect of comproportionation when the second electrontransfer reaction is irreversible and for steady-state voltammetry we have provided explanations for the development of asymmetry in the second wave and the appearance of onset potentials. This, together with the previous research cited above, completes the suite of effects that can be observed when one or more of the above constraints is released.

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