the chloride using thionyl chloride in ether and 1 equiv of tri-*n*-butylamine (78.5% yield),

1-Methoxy-2-methylthioethane-*1,1-d₂* was prepared from ethyl methylthioacetate by reduction with lithium aluminum deuteride to give 2-methylthioethanol-*1,1-d₂* (67% yield) followed by methylation of the alcohol with methyl iodide and silver oxide in dimethylformamide (62% yield). All samples were purified by preparative gas chromatography prior to analysis of their ICR spectra.

References and Notes

(1) (a) C. C. Price and S. Oae, "Sulfur Bonding," Ronald Press, New York, N.Y., 1962; (b) D. J. Cram, "Fundamentals of Carbanion Chemistry", Academic Press, New York, N.Y., 1965; (c) Y. Yano and S. Oae, *Mech. React. Org. Sulfur Compd.*, **4**, 167 (1969).
(2) E. Campaigne, "The Chemistry of the Carbonyl Group", S. Patai, Ed., Interscience, New York, N.Y., 1966, Chapter 17.
(3) F. Bernardi, I. G. Csizmadia, H. B. Schlegel, and S. Wolfe, *Can. J. Chem.*, **53**, 1144 (1975).
(4) L. M. Stock and H. C. Brown, *Adv. Phys. Org. Chem.*, **1**, 35 (1963).
(5) F. G. Bordwell and P. J. Boutan, *J. Am. Chem. Soc.*, **78**, 854 (1956).
(6) F. G. Bordwell, G. D. Cooper, and H. Morita, *J. Am. Chem. Soc.*, **79**, 376 (1957).
(7) T. C. Jones and E. R. Thornton, *J. Am. Chem. Soc.*, **89**, 4863 (1967).
(8) F. H. Field and D. P. Weeks, *J. Am. Chem. Soc.*, **92**, 6521 (1970); D. P. Weeks and F. H. Field, *ibid.*, **92**, 1600 (1970).
(9) A. G. Harrison, A. Ivko, and D. van Raalte, *Can J. Chem.*, **44**, 1625 (1966).
(10) R. H. Martin, F. W. Lampe, and R. W. Taft, *J. Am. Chem. Soc.*, **88**, 1353 (1966).
(11) B. G. Keyes and A. G. Harrison, *J. Am. Chem. Soc.*, **90**, 5671 (1968).
(12) R. W. Taft R. H. Martin, and F. W. Lampe, *J. Am. Chem. Soc.*, **87**, 2490 (1965).
(13) A. G. Harrison, C. D. Finney, and J. A. Sherk, *Org. Mass Spectrom.*, **5**, 1313 (1971).
(14) J. F. Wolf, R. H. Staley, I. Koppel, M. Taagepera, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *J. Am. Chem. Soc.*, **99**, 5417 (1977); see also R. W. Taft in "Proton Transfer Reactions", E. F. Caldin and V. Gold, Ed., Chapman and Hall, London, 1975.
(15) Hydride transfer equilibria have been established in the gas phase by high-pressure mass spectrometry; see J. J. Solomon and F. H. Field, *J. Am. Chem. Soc.*, **98**, 1567 (1976), and references cited therein.
(16) R. T. McIver, Jr., *Rev. Sci. Instrum.*, **49**, 111 (1978).
(17) J. D. Baldeschwieler, *Science*, **159**, 263 (1968); C. J. Drewery, G. C. Goode, and K. R. Jennings, *MTP Int. Rev. Sci.: Phys. Chem., Ser. One* (1972); J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1971).
(18) J. K. Pau, J. K. Kim, and M. C. Caserio, *J. Am. Chem. Soc.*, **100**, 3831 (1978).
(19) Experiments by R. W. Taft and I. Koppel on reaction 5 provide an estimate of ΔG as −2.4 ± 0.5 kcal mol⁻¹ (private communication).
(20) J. K. Kim, M. C. Findlay, W. G. Henderson, and M. C. Caserio, *J. Am. Chem. Soc.*, **95**, 2184 (1973).
(21) J. L. Beauchamp and R. C. Dunbar, *J. Am. Chem. Soc.*, **92**, 1477 (1970).
(22) The difference in exothermicity of reactions 10 and 11 is the difference in the heats of formation of the neutral products, $\Delta H_{\text{fCH}_2\text{O}} + \Delta H_{\text{fCH}_3\text{OCH}_3} - \Delta H_{\text{fCH}_3\text{OCH}_2\text{OCH}_3}$, or (−28 −44 + 71) = −1 kcal. From bond energies, the difference is calculated as −5 kcal.
(23) J. K. Pau, J. K. Kim, and M. C. Caserio, *J. Am. Chem. Soc.*, **100**, 3838 (1978); *J. Chem. Soc., Chem. Commun.*, 121 (1974).
(24) J. L. Beauchamp and T. H. Morton, *J. Am. Chem. Soc.*, **94**, 3671 (1972).
(25) H. Perst, "Oxonium Ions in Organic Chemistry", Verlag Chemie, Academic Press, New York, N.Y., 1971; H. Perst in "Carbonium Ions", Vol. V, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., 1976.
(26) B. Capon, *Q. Rev., Chem. Soc.*, **18**, 45 (1964).
(27) K. Levsen, H. Heimbach, C. C. Van de Sande, and J. Monstrey, *Tetrahedron*, **33**, 1785 (1977). See also B. van de Graaf and F. W. McLafferty, *J. Am. Chem. Soc.*, **99**, 6810 (1977).
(28) The validity of using kinetic methods to evaluate carbocation stabilities has been questioned; see C. D. Johnson, *Chem. Rev.*, **75**, 755 (1975).
(29) D. Martin and H. Niclas, *Chem. Ber.*, **102**, 31 (1969).
(30) R. J. H. Clark and A. J. McAlees, *Inorg. Chem.*, **11**, 342 (1972).
(31) The relation between rate and exothermicity implied in this argument is supported by the work of Ausloos and Lias, who report several reactions where rate constants of hydride abstraction reactions correlate with the exothermicities of the reactions. See S. G. Lias, J. R. Eyler, and P. Ausloos, *Int. J. Mass Spectrom. Ion Phys.*, **19**, 219 (1976); **18**, 261 (1975).
(32) G. Gioumousis and D. P. Stevenson, *J. Chem. Phys.*, **29**, 294 (1958). The specific collision rate is expressed by the equation $k = 2\pi e \, (\alpha/\mu)^{1/2}$ where e is the electronic charge, α is the polarizability of the neutral, and μ is the reduced mass of the ion–molecule pair. In the case of methoxymethylthiomethane, the polarizability was calculated from bond polarizabilities to be 89 × 10⁻²⁵.

Electron Transfer to and from Molecules Containing Multiple, Noninteracting Redox Centers. Electrochemical Oxidation of Poly(vinylferrocene)

James B. Flanagan, Shlomo Margel, Allen J. Bard,[1] **and Fred C. Anson***

*Contribution No. 5674 from the Arthur A. Noyes Laboratory,
California Institute of Technology, Pasadena, California 91125.
Received October 21, 1977*

Abstract: A general analysis is presented of the behavior to be expected in voltammetric experiments with molecules containing a number of identical, noninteracting centers that accept or give up electrons. It is shown that all such molecules will exhibit current–potential responses having the same shape as that obtained with the corresponding molecule containing a single center. Only the magnitude of the current is enhanced by the presence of additional electroactive centers. As an experimental example of the predicted behavior, the electrooxidations of vinylferrocene and two poly(vinylferrocenes) in nonaqueous media are described. A comparison of the behavior predicted in the present work with several previous studies of molecules with multiple redox centers is also presented.

The electrochemical behavior of molecules which contain several electroactive sites has been the subject of a number of studies.[2,3] The differences in potential between the half-reactions of the successive electron transfers to such molecules can depend upon the extent of interaction between the sites, solvation changes, ion pairing, and structural changes of the molecule, but for molecules containing identical, *noninteracting* centers, the successive electron transfers will follow simple statistics. In the absence of significant molecular

reorganization or solvation changes, the separations between successive formal potentials (as defined below) will depend only on the number of centers present. For example, with two centers present the separation is equal to $(RT/F) \ln 4$.[4a] This situation is analogous to that of the separation in pKs of a molecule with noninteracting acidic groups.[5] As Ammar and Savéant have pointed out,[4a] the Nernstian voltammetric wave which results from such a situation has the shape of a one-electron transfer reaction, although more than one electron is

transferred in the overall reaction. In a recent paper[6] on the electroreduction of poly-2-vinylnaphthalene and poly-9-vinylanthracene, evidence was presented for multielectron transfer (up to 1200 electrons per molecule!) producing voltammetric waves with the overall shape of one-electron transfer reactions. Similarly in a recent study of the electrochemical oxidation of poly(vinylferrocene) (PVF) multielectron transfers were observed.[7]

We report here a theoretical analysis of the expected current-potential characteristics for multiple electron transfers to a molecule containing any number of noninteracting redox centers and demonstrate that the statistical factors which govern the behavior produce a current-potential response with Nernstian systems which, except for the larger limiting currents, has all the characteristics of a one-electron transfer reaction. Such behavior is demonstrated by the electrochemical oxidation of PVF for which coulometric measurements are employed to show that the total number of electrons transferred is equal to the number of ferrocene residues present in the molecule.
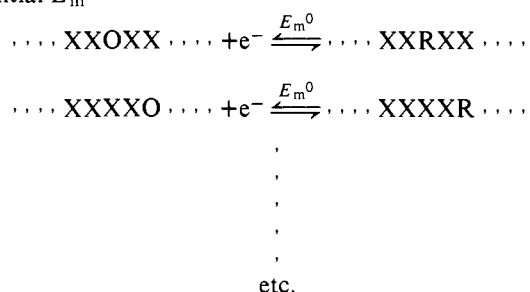
Experimental Section

Reagents. *N,N*-Dimethylformamide (DMF) was stirred over anhydrous copper sulfate for 24 h, distilled under reduced pressure, and stored under argon. Tetrahydrofuran (THF) was refluxed over sodium for 24 h, distilled under reduced pressure, and stored under argon. Polarographic grade tetra-*n*-butylammonium perchlorate (TBAP) (Southwestern Analytical Chemicals, Austin, Texas), used as supporting electrolyte, was used as received after drying under vacuum. The samples of poly(vinylferrocene) were generously donated by Dr. Thomas W. Smith (Xerox Corp.); the synthesis, purification, and measurement of molecular weights of these samples have been described.[7]

Apparatus. Cyclic voltammetry and coulometry experiments were carried out with a PAR Model 173 potentiostat (Princeton Applied Research Corp., Princeton, N.J.) driven by a PAR Model 175 programmer. Current–voltage curves were recorded on a Tektronix Model 564 oscilloscope or an X–Y recorder. Pulse polarography studies were performed with a PAR Model 174 instrument.

A conventional three-electrode cell was used in all experiments. The working electrode for voltammetric experiments was a platinum sphere with an area of 3.0 mm³. For coulometry a large platinum gauze electrode was employed. The reference electrode was a silver wire immersed in the test solution but isolated from the main chamber by a sintered-glass disk. The potential of this reference electrode was not particularly stable. Its potential was measured with respect to an aqueous saturated calomel electrode (SCE) to obtain the values of potential on this scale. The counter electrode was platinum and was isolated in a separate chamber of the cell. Positive feedback techniques were employed to minimize the effects of uncompensated resistance in the cyclic voltammetric measurements.

Theory of Electron Transfer with Reactants Having Multiple Electroactive Centers

Consider a polymeric molecule containing n independent centers capable of accepting or donating one electron. Suppose that each center has the same standard potential, E_m^0, and adheres to the Nernst equation independently of the oxidation state of any of the other centers in the molecule; i.e., for each center there is a corresponding half-reaction with standard potential E_m^0

$$\cdots XXOXX \cdots + e^- \underset{\overleftarrow{}}{\overset{E_m^0}{\rightleftharpoons}} \cdots XXRXX \cdots$$

$$\cdots XXXXO \cdots + e^- \underset{\overleftarrow{}}{\overset{E_m^0}{\rightleftharpoons}} \cdots XXXXR \cdots$$

,
,
,
,
,

etc.

where O and R represent the electroactive center in its oxidized and reduced states, respectively, and X represents a center in either oxidation state. At equilibrium the probability that any site, i, is reduced is given by

$$P(i = R) = \frac{1}{1 + \theta} \tag{1}$$

where

$$\theta \equiv \exp\left[\frac{F}{RT}(E - E_m^0)\right] \tag{2}$$

and E is the potential of an electrode with which the multiple-centered molecule is in equilibrium.

The "oxidation state" of such a polymeric molecule amounts to the sum of the monomeric components of the molecule that are in their oxidized states, namely, $(n - j)$, where j is the number of reduced sites. Application of standard probability theory[8] leads straightforwardly to a binomial distribution of the various forms of partially reduced polymer:

$$f_j = \binom{n}{j}\left(\frac{\theta}{1 + \theta}\right)^{(n-j)}\left(\frac{1}{1 + \theta}\right)^j \tag{3}$$

where f_j is the fraction of the polymer molecules present containing exactly j reduced centers (and $(n - j)$ oxidized centers) at each value of θ and

$$\binom{n}{j} \equiv \frac{n!}{j!\,(n - j)!}$$

$\theta/(1 + \theta)$ and $1/(1 + \theta)$ are the probabilities that any particular monomeric center is oxidized or reduced, respectively.

If C_p is the bulk concentration of polymer, the equilibrium concentration, C_j, of molecules containing exactly j reduced sites (produced, for example, by controlled potential electrolysis of the solution at potential E) is given by

$$C_j = C_p f_j \tag{4}$$

where f_j has the value corresponding to potential E. In many cases (discussed below) the same expression may be used to calculate concentrations at the electrode surface in voltammetric experiments.

Figure 1A shows calculated fractional concentration-potential curves for the reduction of a two-center molecule. The three curves represent the fractions, f_0, f_1, and f_2, of unreduced, half-reduced, and fully-reduced molecules, respectively. The curves intersect at the potentials where $f_0 = f_1$ and $f_1 = f_2$, i.e., at the formal potentials for the two redox couples present. These are identified in Figure 1 as E_1^F and E_2^F. The difference between these two intersection potentials is 35.6 mV (at $T = 297$ K), a result which has been discussed previously for molecules with two noninteracting centers by Ammar and Savéant.[4a] For the general case of molecules containing n noninteracting reducible centers it is possible to calculate the formal potentials corresponding to each pair of successive oxidation states of the polymer by noting that at E_j^F, $f_j = f_{(j-1)}$.[4b]

Application of eq 2 and 3 then leads to

$$E_j^F = E_m^0 - \frac{RT}{F}\ln\left[\frac{j}{n - j + 1}\right] \tag{5}$$

As an example, Figure 2 illustrates fraction–potential and current–potential curves calculated for $n = 5$.

The difference between the formal potentials for the first and last pair of oxidation states in a molecule with n reducible centers is logarithmically related to n:

$$E_1^F - E_n^F = (2RT/F)\ln n \tag{6}$$

For large n, this means that there will be large overlap of the concentrations of the various partially reduced species at po-
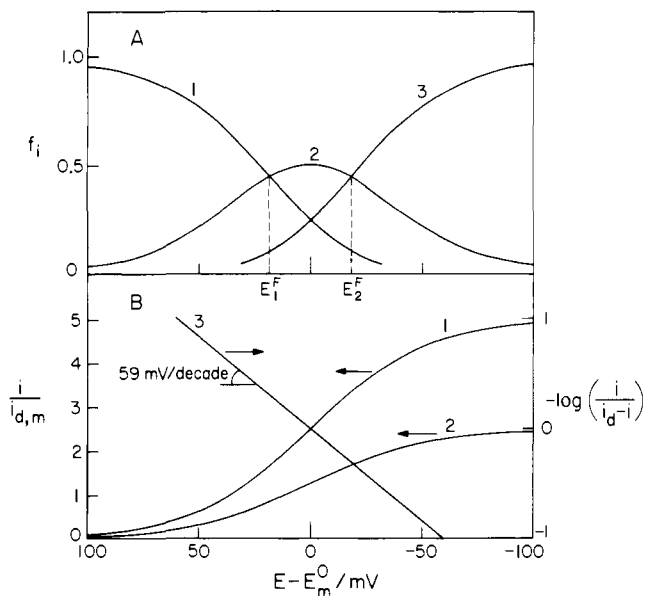
Figure 1. Calculated fractional concentration–potential and current–potential curves for a reactant with two reducible centers. (A) Fractional concentrations of unreduced (1), half-reduced (2), and fully reduced (3) reactant. E_1^F and E_2^F are the formal potentials corresponding to the transfer of the first and second electrons to the molecule, respectively. (B) Current–potential curves for equal concentrations of (1) one-center and (2) two-center reactants. The currents have been corrected for differences in the diffusion coefficients of the one-center and two-center reactants. $i_{d,m}$ is the diffusion limited current for the one-center molecule. Curve 3 is the plot of $-\log i/(i_d - i)$ for both current–potential curves. A temperature of 25 °C is assumed.

tentials in the rising portion of a polarization curve, i.e., that the successive formal potentials will fall increasingly close to each other as n increases. Note that the spacing between successive formal potentials becomes nonuniform for $n \geqslant 4$.

Comparison of the A and B portions of Figures 1 and 2 reveals that the half-wave potential obtained with polymeric molecules matches the half-wave potential obtained with the corresponding molecule with one center and falls at the formal potential $E_{(n+1)/2}^F$ when n is odd. For even values of n, the half-wave potential falls between $E_{n/2}^F$ and $E_{(n+2)/2}^F$.

To calculate $Q_n(\theta)$, the total number of electrons consumed by a polymeric reactant of n centers during electrolysis from the completely oxidized state at a potential corresponding to θ, we multiply the amount of each reduced species formed by the number of electrons it has accepted and sum for all j:

$$Q_n(\theta) = FN_T \sum_{j=0}^{n} jf_j \qquad (7)$$

where N_T is the total number of moles of polymer taken and F is the Faraday.

Under conditions where eq 4 applies to concentrations at the electrode surface during voltammetric experiments, the *shapes* of the current–potential curves obtained may be calculated with the aid of eq 7. (The *magnitudes* of currents will, of course, be scaled by diffusion coefficients and the experimental parameters applicable to each technique.) Voltammetric techniques in which the surface concentrations of reactant and product are directly reflected in the current–potential curves include dc polarography, normal pulse polarography, and voltammetry at rotating disk electrodes.

It can be shown that the shape of the current–potential curves obtained with these techniques will have the same shape as the corresponding curve for the species containing only a single reducible center but the limiting currents will be larger by a factor of n, the degree of polymerization. In terms of eq
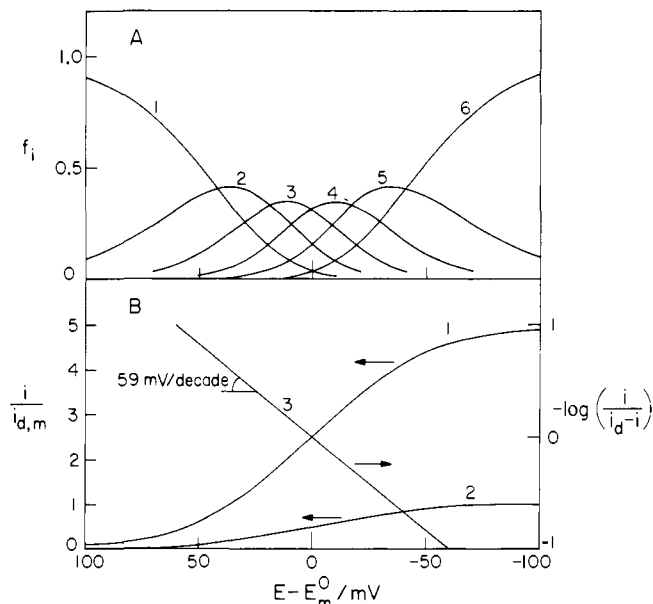

Figure 2. Calculated fractional concentration–potential and current–potential curves for a reactant with five reducible centers. The numbered curves have the corresponding significance to those identified in Figure 1.

7 this correspondence can be expressed as

$$Q_n(\theta) = nQ_1(\theta) \qquad (8)$$

Equation 8 can be shown to be an identity by substituting eq 7 into both sides and performing a few manipulations.

The corresponding current–potential identity is

$$i_n(\theta) = ni_1(\theta) \left(\frac{D_p}{D_m}\right)^p \qquad (9)$$

where i_n is the current obtained at each value of θ with a polymer and i_1 the corresponding current for a monomeric sample when the concentrations of both polymer and monomer are equal. D_p and D_m are diffusion coefficients for polymer and monomer, respectively, and the exponent p depends on the voltammetric technique employed.

Figures 1B and 2B show the current–potential curves calculated for the reduction of two-center and five-center molecules, respectively, along with the corresponding plots of log $i/(i_d - i)$ vs. potential. The latter pair of plots, whose slopes reflect the steepness of the rising portions of the current–potential curves, are indistinguishable from each other and are identical with the plot that would result for the reduction of a monomeric one-electron reactant. Thus, the magnitudes but not the shapes of the current–potential curves are affected by the number of noninteracting reducible centers the reactant contains.

The current–potential responses obtained with techniques such as cyclic voltammetry, differential pulse polarography, and ac polarography bear a more complex relation to the concentrations of reactant and product at electrode surfaces so that simple equations analogous to eq 8 and 9 are not available. However, the shapes of cyclic voltammograms are discernible from those of corresponding polarographic or steady-state current–potential curves by means of semidifferentiation.[9a] In this way it can be shown that cyclic voltammograms (as well as differential pulse and alternating current polarograms) for molecules with multiple, noninteracting redox centers will also exhibit shapes that match those of the corresponding species with a single center. Thus, the anodic and cathodic peak potentials and the peak and half-peak potentials should both be separated by 58 mV (25 °C).[10]
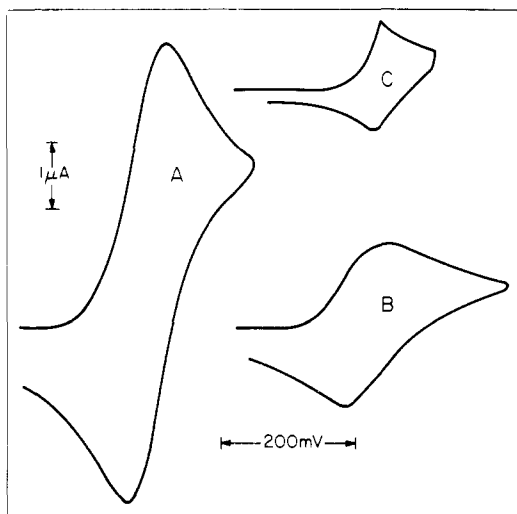
Figure 3. Cyclic voltammograms for vinylferrocene (VF) and poly-(vinylferrocene) (PVF) in 10 mL of DMF as solvent. (A) 1.0 mg VF (mol wt 212); (B) 1.2 mg PVF of mol wt 4930; (C) 1.0 mg PVF of mol wt 15 750. The initial potential for all voltammograms was +250 mV vs. the silver wire reference electrode. More oxidizing potentials are to the right; oxidation currents are plotted upward. Supporting electrolyte: 0.1 M TBAP. Scan rate: 100 mV s^{-1}.

Figure 4. Cyclic voltammograms for poly(vinylferrocene) in 10 mL of THF as solvent. (—), 0.94 mg of PVF of mol wt 4930; (- - -), 0.9 mg of PVF of mol wt 15 750. The initial potential was +100 mV vs. the silver wire reference electrode. More oxidizing potentials are to the right. Oxidation currents are plotted upward. Supporting electrolyte: 0.2 M TBAP. Scan rate: 100 mV s^{-1}.

The peak currents of cyclic voltammograms for polymeric reactants will obey eq 9 with $p = \frac{1}{2}$. This is true despite the fact that in the equation for the voltammetric peak current with Nernstian reactants n, the number of electrons transferred, appears with the exponent $\frac{3}{2}$, not 1.[10] The reason is that the equation for the peak current is derived for an electrode reaction in which n electrons are assumed to be transferred essentially simultaneously while the type of multicentered reactant we have been discussing undergoes n successive, one-electron transfers per molecule.

Departures from Simple Theory. A variety of factors could cause departures from the behavior calculated on the basis of the simple model employed thus far: interactions between adjacent reducible centers; slow electron transfer at the electrode, i.e., non-Nernstian behavior; structural changes in the polymer which accompany its reduction; adsorption or precipitation of reactants or products at the electrode surface; or changes in diffusion coefficients of reactants and products as charge is added or removed from the polymer.

The variety of experimental examples[11] in which molecules bearing several identical reducible (or oxidizable) centers exhibit multiple waves at separate potentials rather than a single, larger wave is presumably a result of one or more of these factors. However, electronic interaction between two centers seems most likely to be the major source of wave splitting.

There are also cases in which the current–potential curves for a multicentered reactant have slopes even greater than that for a one-electron reactant.[3] This can occur when the addition of the first electron produces a species which accepts additional electrons more readily than the original reactant. Simulated voltammograms corresponding to a variety of conditions have been discussed by Polcyn and Shain.[12]

Experimental Results and Discussion

Voltammetric Studies. As discussed by Smith et. al.,[7] finding a solvent in which PVF and its oxidation products are adequately soluble and in which adsorption or precipitation of reactants or products does not distort cyclic voltammograms is difficult. We had the best success with DMF and THF. With DMF it was necessary to heat the DMF–polymer mixture to
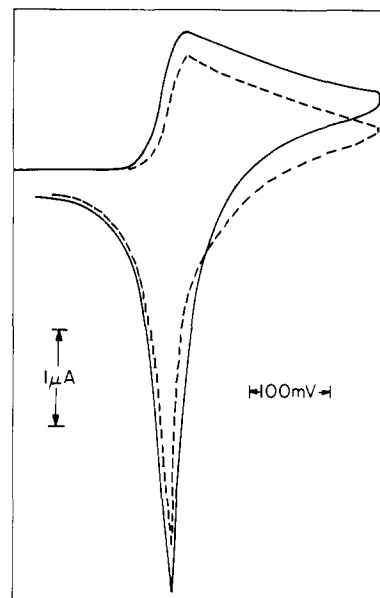
150 °C and then cool slowly to room temperature to dissolve milligram amounts of PVF. Typical cyclic voltammograms of the monomer, vinylferrocene (VF), and PVF are shown in Figure 3. In both DMF and THF the wave for VF shows characteristics of a reversible one-electron transfer with production of a soluble, stable product, i.e., $i_{pa}(v)^{-1/2}$ and E_{pa} independent of scan rate, $E_{pa} - E_{pc} \sim 60$ mV, and $i_{pc}/i_{pa} \sim 1$ (where i_{pa} and i_{pc} are the peak anodic and cathodic currents, respectively, E_{pa} and E_{pc} are the anodic and cathodic peak potentials, and v is the scan rate). In DMF the 5 K polymer exhibits generally similar characteristics, but the 16 K PVF shows evidence of adsorption of the reactant in the form of overly sharp anodic peak currents (Figure 3). For THF solutions adsorption of the reactant was not observed (i.e., i_{pa}, $(v)^{-1/2}$ was independent of v) but the cathodic wave on scan reversal showed that the oxidized product had accumulated at the electrode surface (Figure 4). Smith et al.[7] noticed similar behavior with methylene chloride as a solvent.

While the cyclic voltammetric behavior of the 5 K polymer in DMF shows the shape and peak separation expected of a reversible one-electron transfer, the adsorption and precipitation problems led us to use normal pulse voltammetry[13] as a means of determining the wave shape parameters and estimating the total number of electrons transferred per polymer molecule. In this technique adsorption or precipitation of the oxidized product should be of less importance, since a smaller amount will accumulate on the electrode surface during the brief pulse duration ($\sim$50 ms) and the oxidized product is reduced back to starting material during the time between pulses when the electrode is held at a potential at the foot of the anodic wave.[14] Typical normal pulse voltammograms are shown in Figure 5 for both VF and PVF in THF. The limiting diffusion currents (i_d), slopes of E vs. log $(i_d - i)/i$ plots, and half-wave potentials ($E_{1/2}$) obtained from the normal pulse polarograms are given in Table I.

The total number of electrons transferred in the oxidation wave for the polymer (n_p) can be estimated from the limiting currents and approximate relative values of the diffusion coefficients of the monomer (D_m) and polymer (D_p).[6] From

Table I. Results of Normal Pulse Voltammetric Oxidation of Vinylferrocene and Poly(vinylferrocene)[a]

Compd	Amount taken, mg	Mol wt	Degree of polymerizn	i_d, μA	C, μM	n_p[b]	Log plot slope,[c] mV	$E_{1/2}$,[d] V vs. SCE
VF	0.57	212	1	9.6	260		61	0.56
PVF	0.55	4930	23.2	3.1	11	18	58	0.46
PVF	0.96	4930	23.2	6.1	19	21	60	0.45
PVF	0.54	15 750	74.3	2.3	4	51	70	0.44
PVF	2.0	15 750	74.3	10.6	12	75	66	0.48

[a] Experimental conditions are given in the caption to Figure 5. [b] Calculated using eq 11. [c] Slope of plot of E vs. log $(i_d - i)/i$. [d] The potential of the silver wire reference electrode employed was reproducible to only ca. ± 50 mV but these potentials were subsequently confirmed (± 15 mV) in experiments where an SCE reference electrode was employed.
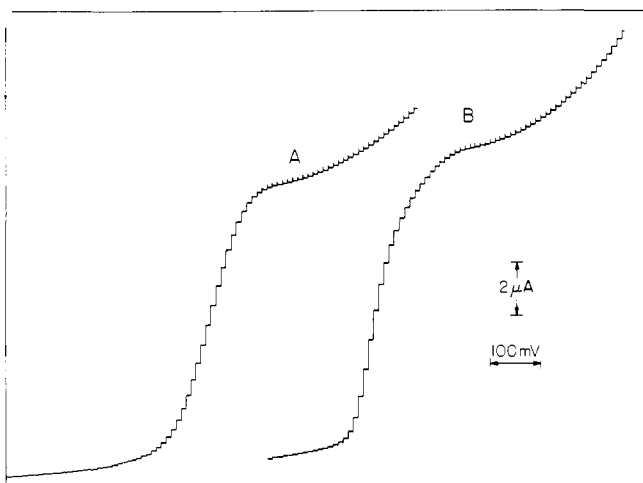

Figure 5. Normal pulse voltammograms for the oxidation of vinylferrocene (VF) and poly(vinylferrocene) (PVF) in 10 mL of THF is solvent. (A) 0.57 mg of VF (mol wt 212); (B) 2.0 mg of PVF of mol wt 15 750. The initial potential was 0 mV vs. the silver wire reference electrode for both polarograms. Supporting electrolyte: 0.2 M TBAP. Scan rate, 2 mV s^{-1}; "drop time", 5 s.

previous work on the relation between diffusion coefficient and molecular weight (M_m or M_p for monomer and polymer, respectively) the following relation seems most appropriate.[15]

$$D_p/D_m = (M_m/M_p)^{0.55} \qquad (10)$$

Assuming that the oxidation of VF is a one-electron reaction the value of M_p can be estimated by employing an equation derived previously for conventional dc polarography:[6]

$$n_p = \frac{(i_{dp}/C_p)}{(i_{dm}/C_m)} \left(\frac{M_p}{M_m}\right)^{0.275} \qquad (11)$$

Values of n_p obtained in this way (Table I) come close to matching the degree of polymerization of the polymer (DP), as was previously found for the reduction of poly-2-vinyl-naphthalene and poly-9-vinylanthracene.[6] Thus, the overall reaction results in the oxidation of essentially every ferrocene center in the PVF molecules. Smith and co-workers[7] made a similar estimation of n_p from the anodic limiting currents in voltammetry at a rotating disk electrode with PVF in hexamethylphosphoramide. They assumed that the Stokes–Einstein equation applied (i.e., D $\sim (M)^{-1/3}$) and reported values of DP/n_p which varied between 1.4 and 4.1 for PVF of different molecular weights. If their data are reanalyzed on the basis of eq 10, we calculate values of DP/n_p which are more nearly constant but still vary from 1.3 to 2.6.

Note that the slopes of the logarithmic plots in Table I are quite close to the values corresponding to Nernstian, multielectron transfers to noninteracting groups in accord with the theoretical treatment presented above. Similar slopes were also

Table II. Results of Controlled Potential Coulometric Oxidation of Poly(vinylferrocene)[a]

Compd	Amount taken, mg	Mol wt	Degree of poly-merizn	Q_a,[b] C	n_p[c]	Q_c,[d] C
PVF	5.10	4930	23.2	2.3$_5$	23.6	1.9
PVF	4.92	15 750	74.3	2.2	73.1	1.3$_5$
PVF	0.94	15 750	74.3	0.43$_5$	75.1	0.21

[a] The electrolysis solution was ca. 15 mL of THF containing 0.2 M TBAP. [b] Charge consumed in the oxidation at +0.35 V VS/ Ag reference electrode ($E_{1/2}$ was ca. 0.2 V vs. this reference electrode). [c] $n_p = Q_a$/mol PVF. [d] Charge consumed in reduction of the oxidized solution at +0.1 V.

observed in the rotating disk voltammetric studies at low concentrations of PVF.[7]

The difference in the values of $E_{1/2}$ for VF and PVF in Table I are not unexpected because the equivalence of $E_{1/2}$ values for polymeric and single-centered molecules predicted in the Theoretical Section assumed a comparison between the polymer and "the corresponding molecule with a single center". A better comparison of $E_{1/2}$ values would be of PVF with monoethylferrocene. Monoethylferrocene has an $E_{1/2}$ value 80 mV more positive than VF in acetonitrile as solvent.[9b] Subtracting 80 mV from the $E_{1/2}$ value for VF in Table I brings it quite close to the observed values for PVF in good accord with the theoretical prediction.

Coulometric Studies. To confirm the magnitude of the multielectron transfers which occur in the oxidation of PVF without the need to estimate diffusion coefficients, coulometric oxidations of PVF at a large area platinum gauze electrode were carried out. The results are summarized in Table II. Note that the n_p calculated from the total coulombs consumed in the oxidation (Q_a) is very close to DP in agreement with the voltammetric results. The higher values of DP/n_p found by Smith et al.[7] in hexamethylphosphoramide as solvent (even when the diffusion coefficient is given the smaller value resulting from eq 10) may be due to differences in the nature of the solvents employed which could lead to considerable differences in the extent of ion pair formation.

If a controlled potential reduction of the oxidized polymer is performed immediately following its oxidation the amount of charge required is less than was consumed during the oxidation. This is probably caused by precipitation of the oxidation product not all of which redissolves during the reduction step in THF. During the oxidation of the bright orange PVF a small amount of green, solid oxidation product is formed which persists following the reduction step.

Comparison with Results of Other Studies. It is of interest to contrast the results presented here for PVF with those that have been reported for several biferrocenes by Morrison et al.[11b] and for 1,1'-polyferrocenes by Brown et al.[11d] In the

former study, single polarographic waves were obtained with diffusion currents corresponding to a two-electron process when certain bridging groups connected the two ferrocene centers (Hg, C_2H_4, $(CH_3)_2CC(CH_3)_2$, and $-CH=CH-C_6H_4CH=CH-$) but separated waves with one-electron diffusion currents resulted with other bridging groups. The slopes of plots of $\log i/(i_d - i)$ vs. potential for the biferrocenes which exhibited a single wave were 80–90 mV, which matched the slope obtained with ferrocene itself. The authors, expecting the slope to be half as large for the biferrocenes as for ferrocene, explained the larger values in terms of electrochemical irreversibility. The present treatment shows that their data are entirely compatible with comparable reversibility for both ferrocene and the biferrocenes; polarographic waves with one-electron slopes and two-electron diffusion currents are to be expected if the two ferrocene centers do not interact strongly. That diferrocenylethane exhibits such behavior is consistent with the results reported here for PVF since the ferrocene centers are separated by the same C_2H_4 bridging group in both cases.

In the previous electrochemical study of the oxidation of 1,1′-polyferrocenes[11d,h] the successive ferrocene groups are oxidized in a series of resolvable waves with values of $E_{1/2}$ separated by hundreds of millivolts. In these molecules the polymer chain is formed by direct linkage of the cyclopentadiene rings so that it is not surprising that strong interaction between the ferrocene residues apparently occurs. This is also suggested by the finding that the ease of oxidation of polyferrocene increases with chain length, i.e., the $E_{1/2}$ values for the first electron transfer increase in the order 1,1′-quaterferrocene < 1,1′-terferrocene < biferrocene < ferrocene. For the PVF molecules the $E_{1/2}$ values are quite close to that for monoethylferrocene, as is expected (vida supra) when the ferrocene centers do not interact significantly.

Conclusion

Electron transfer to or from polymeric molecules containing identical, noninteracting electroactive centers will involve as many electrons as there are centers and will yield a voltammetric wave with a shape matching that of the corresponding molecule with a single electroactive center but with a magnitude determined by the total number of centers present. This conclusion assumes the absence of complications arising from adsorption, precipitation, or slow electron transfer kinetics.

References and Notes

(1) Department of Chemistry, The University of Texas, Austin, Texas 78712.
(2) A. J. Bard, *Pure Appl. Chem.*, **25**, 379 (1971), and references cited therein.
(3) F. Ammar and J. M. Savéant, *J. Electroanal. Chem.*, **47**, 115 (1973), and references cited therein.
(4) (a) F. Ammar and J. M. Savéant, *J. Electroanal. Chem.*, **47**, 215 (1973). (b) It is important to note the difference between E_m^0 and E_f^f. The latter is the potential at which the sum of all microscopic forms of a molecule having oxidation state j is equal to the sum of all forms having oxidation state $j - 1$. The former is the common standard potential relating each microscopic center that is in its oxidized state to its reduced counterpart no matter what the overall oxidation state of the polymeric molecule happens to be.
(5) S. W. Benson, *J. Am. Chem. Soc.*, **80**, 515 (1958).
(6) T. Saji, N. F. Pasch, S. E. Webber and A. J. Bard, *J. Phys. Chem.*, in press.
(7) T. W. Smith, J. E. Kuder, and D. Wychick, *J. Polym. Sci.*, **14**, 2433 (1976).
(8) M. R. Spiegel in "Statistics", McGraw-Hill, New York, N.Y., 1961, p 122.
(9) (a) J. C. Imbeaux and J. M. Saveant, *J. Electroanal. Chem.*, **44**, 169 (1973); M. Goto and K. B. Oldham, *Anal. Chem.*, **45**, 2043 (1973); (b) T. Kuwana, D. E. Bublitz, and G. Hoh, *J. Am. Chem. Soc.*, **82**, 5211 (1960).
(10) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).
(11) E.g., (a) S. A. Adeyemi, J. N. Braddock, G. M. Brown, J. A. Ferguson, F. J. Miller, and T. J. Meyer, *J. Am. Chem. Soc.*, **94**, 300 (1972); (b) W. H. Morrison, Jr., S. Krogsrud, and D. N. Hendrickson, *Inorg. Chem.*, **12**, 1998 (1973); (c) C. LeVanda, D. O. Cowan, C. Leitch, and K. Beckgaard, *J. Am. Chem. Soc.*, **96**, 6788 (1974); (d) G. M. Brown, T. J. Meyer, D. O. Cowan, C. LeVanda, F. Kaufman, P. V. Roling, and M. D. Rausch, *Inorg. Chem.*, **14**, 506 (1975); (e) G. M. Tom and H. Taube, *J. Am. Chem. Soc.*, **97**, 5310 (1975); (f) M. J. Powers, R. W. Callahan, D. J. Salmon, and T. J. Meyer, *Inorg. Chem.*, **15**, 894 (1976); (g) R. W. Callahan, F. R. Keene, T. J. Meyer, and D. J. Salmon, *J. Am. Chem. Soc.*, **99**, 1064 (1977); (h) C. Levanda, K. Beckgaard, D. O. Cowan, and M. D. Rausch, *ibid.*, **99**, 2964 (1977).
(12) D. S. Polcyn and I. Shain, *Anal. Chem.*, **38**, 370 (1966).
(13) E. P. Parry and R. A. Osteryoung, *Anal. Chem.*, **37**, 1634 (1965).
(14) J. A. Turner, R. H. Abel, and R. A. Osteryoung, *Anal. Chem.*, **47**, 1343 (1975).
(15) C. Tanford in "The Physical Chemistry of Macromolecules", Wiley, New York, N.Y., 1961, p 362.