Coordination Chemistry Reviews, 93 (1989) 1–18
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

APPLICATION OF MICROELECTRODES AND VARIABLE-TEMPERATURE TECHNIQUES TO VOLTAMMETRIC STUDIES OF INORGANIC REACTION MECHANISMS

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(Received 10 May 1988)

CONTENTS

ABBREVIATIONS

TPP	dianion of tetraphenylporphyrin
PP	dianion of protoporphyrin IX
PPDME	dianion of protoporphyrin IX dimethyl ester
OEP	dianion of octaethylporphyrin
MeIm	*N*-methylimidazole
$k(E)$	heterogeneous charge transfer rate constant as a function of potential
k_s	standard heterogeneous charge transfer rate constant ($E = E^0$).

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0010-8545/89/$6.3

SUMMARY

Two important developments in voltammetric methodology are discussed in this article. These are (1) the ready accessibility of large temperature ranges both above and below ambient and (2) the introduction of microelectrodes which are several orders of magnitude smaller than conventional electrodes. These developments, in effect, allow the chemist to vary the time domain of the experiment, which is quite useful for the detection of transients and the determination of heterogeneous charge transfer rate constants as well as rate constants of homogeneous reactions coupled to the charge transfer. Experiments with a variety of metalloporphyrin complexes are presented to show how voltammetry at variable temperature and with microelectrodes can be conveniently used to probe reaction mechanisms.

A. INTRODUCTION

The past decade has seen a substantial increase in the popularity of voltammetric techniques as applied to inorganic chemistry. Voltammetry at stationary electrodes, in particular, is now routinely used by many research groups to characterize the redox properties of new compounds. Equally important, and perhaps more interesting, is the recent increase in the use of electrochemistry to induce or promote inorganic reactions (stoichiometric and catalytic) such as ligand substitution, ligand migration, and oligomerization [1]. Especially in the organometallic area, a number of these electroactivated reactions proceed with amazing speed, yield, and selectivity when compared with the analogous non-radical thermally driven reactions.

Electrochemistry can also be a powerful tool with which to investigate the mechanisms of inorganic reactions. Qualtitatively, voltammetric experiments may be used to identify redox-active reaction intermediates (and products) and estimate their stability. In suitable cases a more quantitative treatment is possible and rate and equilibrium constants can be extracted. Using metalloporphyrin complexes as examples, we show in this paper how cyclic voltammetry at variable temperatures (+100 to −100°C) and with electrodes of variable size (1 mm–1 μm diameter) can be conveniently used to obtain mechanistic information.

When studying a redox process using a voltammetric technique one needs to be concerned about the electrochemical reversibility (or rate) of the heterogeneous electron transfer as well as the chemical reversibility (or rate) of any coupled homogeneous chemical reactions. Heterogeneous electron transfer is reversible when it occurs rapidly on the time scale of the voltammetric experiment; in this case the Nernst equation is obeyed at the electrode surface and the $E_{1/2}$ ($\approx E^0$) value obtained is directly related to the thermodynamics of the process. Kinetics have an observable influence on the current vs. potential response (including the $E_{1/2}$ value) when the electron transfer is not suitably rapid; in this case the data can, in principle, be used to determine the heterogeneous charge transfer rate constant, $k(E)$, which depends exponentially on the applied potential [2]. The standard heterogeneous charge transfer rate constant, k_s, is the value of $k(E)$ when $E = E^0$. When k_s is sufficiently small so that the charge transfer can occur in one direction only (reduction or oxidation) at a given applied potential, the process is termed electrochemically irreversible. Charge transfer that is too slow to be treated as reversible but too fast to be irreversible is quasi-reversible. It is best to avoid quasi-reversible behavior (by altering the time domain of the experiment, vide infra) because it is often more difficult to treat this case theoretically.

The presence of homogeneous chemical reactions coupled to the heterogeneous charge transfer process may influence the results, depending on the experimental time scale. This is conveniently illustrated by the common EC mechanism, which involves electron transfer followed by chemical reaction of the electrogenerated species. An example of an EC mechanism is given by eqn. (1):

$$\mathrm{O} + ne^- \overset{k(E)}{\rightleftharpoons} \mathrm{R} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{X} \tag{1}$$

in which O is an electroactive species in the bulk solution that is reduced at the electrode to R, which in turn can react chemically to give X. If the chemical (C) step is very slow (small k_1), it will not proceed detectably during the experiment and the current–potential response is unaffected by its presence; in this case the voltammogram is said to be chemically reversible, and a cyclic voltammogram (CV) at an electrode of conventional size will have a fully developed wave for the oxidation of the electroactive species (R) generated on the forward (negative) scan. The CV will also be chemically reversible if the homogeneous reaction is very rapid in both directions (large k_1 and k_{-1}); in this case the fully reversible waves for the E couple are shifted along the potential axis by an amount dependent on the equilibrium constant of the chemical step. However, if the homogeneous reaction is rapid in the forward direction only so that it is essentially unidirectional rather than bidirectional (e.g. as with many decomposition reactions) the CV will be chemically irreversible, meaning that the wave on the reverse scan is absent. Of course, intermediate cases are also possible in which the kinetics of the chemical step lead to partially reversible behavior. In all but the fully reversible cases, an appropriate analysis of the voltammetric data may provide rate constants for the homogeneous reactions.

A variety of time scales are available in voltammetric experiments with conventional electrodes (e.g. sphere or disk having a radius of 1–10 mm). These range from long (slow) in d.c. polarography (drop time, 0.5–5 s) to much shorter in cyclic, rotating disk, and a.c. voltammetry. The time domain may be tuned to the chemical system under study by changing the appropriate experimental parameter (sweep rate, rotation rate, a.c. frequency). However, when using conventional electrodes, there are significant limitations on the range these parameters may assume without introducing complications. The most common and serious complications in short time domain experiments are due to charging current and distortion due to uncompensated solution resistance (*iR* drop). The *iR* drop distortion may be particularly severe in relatively nonpolar organic solvents such as acetone and dichloromethane. In order to probe the kinetics of heterogeneous electron transfer as well as to study rapid coupled homogeneous (bidirectional) chemical steps, it is generally necessary to have a time scale short enough so that the processes are at least partially irreversible. This in turn is often made difficult by the complications just mentioned, both of which become more serious as the scan rate is increased. Even when "corrections" are applied, e.g. positive feedback compensation, rate constants obtained under short time domain conditions with conventional electrodes may be quite inaccurate. For example, it now appears [3–5] that the k_s value for the oxidation of ferrocene in weakly polar solvents has been underestimated by more than an order of magnitude. Other examples of (published) incorrect electron transfer rate constants are becoming evident. Fortunately, recent advances in microelectrode technology now make it possible to use very short time domains and obtain relatively distortion-free data, thus allowing k_s values to be determined with greater accuracy.

The recent development [6] of platinum, gold, and carbon disk microelectrodes with diameters less than 50 μm promises to have a major impact on mechanistic inorganic chemistry. Microelectrodes offer several significant advantages over conventional electrodes (radius $\geqslant$ 1 mm) in linear sweep voltammetric experiments. A smaller *RC* time constant and greatly reduced *iR* distortion allow scan rates in excess of 100000 V s^{-1} in organic solvents [4,7]. In contrast, the use of scan rates above ca. 100 V s^{-1} is impractical with conventional electrodes in organic solvents. With access to the short time domains possible with microelectrodes, very rapid reactions that normally appear to be reversible approach electrochemical (or chemical) irreversibility, hence allowing kinetic (mechanistic) information to be obtained using the same theory available for electrodes of conventional size.

A particularly attractive feature of microelectrodes is the readily accessible steady state current response at low sweep rates (ca. 20 mV s^{-1}), which is due to the predominance of radial (convergent) diffusion under these conditions. The current is proportional to the electrode edge or radius and not the area. The steady state condition produces minimal iR distortion and virtually eliminates the interfering capacitative charging current. Furthermore, the time domain can also be adjusted, not by varying the sweep rate, but by varying the electrode size. For example, whether or not an electrode process appears electrochemically reversible depends on the relative rates of mass transport (diffusion) and charge transfer. As the electrode size is decreased the mass transport rate increases, so that the kinetics of charge transfer may become important or even limiting (electrochemically irreversible condition) if the microelectrode is small enough. The important parameters are k_s and D/r, where D is the diffusion coefficient of the electroreactant and r is the electrode radius. If $k_s \gg D/r$, the charge transfer will be reversible, and if $k_s \ll D/r$, it will be irreversible [8]. It follows that electron transfers that are reversible in d.c. experiments at conventional electrodes may be rendered irreversible (and hence subject to mechanistic study) by using microelectrodes of the appropriate size. Recent theoretical advances show how steady state voltammetry with microelectrodes can be used to measure rapid heterogeneous and homogeneous rate constants [8,9]. When the theory is fully elaborated and available, steady state voltammetry with microelectrodes should prove to be a powerful tool for the inorganic chemist.

The reversibility of heterogeneous and homogeneous chemical reactions may also be affected by changing the rate (and equilibrium) constants. This can be accomplished most conveniently by varying the temperature. With appropriate solvents, temperature ranges of several hundred degrees are now accessible for voltammetric studies. Over temperature ranges of this size, rate constants generally vary by several orders of magnitude. Hence, for a fixed voltammetric time domain, thermodynamics (reversible) or kinetics (irreversible) may be made to control the current response. Experiments at low temperature have additional advantages in that it is possible (1) to study thermally unstable complexes prepared chemically at low temperatures and (2) to detect transients produced electrochemically. Herein we report the use of metalloporphyrin complexes to illustrate how variation of the experimental time domain via the use of microelectrodes and variable temperatures may be used for mechanistic studies in inorganic chemistry.

B. EXPERIMENTAL

(i) Chemicals

Hemin chloride, Fe(PP)Cl, was esterified to the dimethyl ester using a published method [10] to give Fe(PPDME)Cl, which was purified by recrystallization from a dichloromethane–pentane mixture. Tetraphenylporphinatoiron(III) chloride, Fe(TPP)Cl, was synthesized from $[Fe(TPP)]_2O$ by a standard procedure [11]. $Fe(TPP)N_3$ and Cr(TPP)Cl were prepared as previously described [12,13]. Butyronitrile was purified by passage through activated alumina followed by fractional distillation from CaH_2. Dichloromethane was freshly distilled under nitrogen from CaH_2. *N*-Methylimidazole, MeIm, was dried over crushed KOH and then distilled from CaH_2 and stored over molecular sieves. Tetrabutylammonium perchlorate, TBAP, was recrystallized from acetone–diethyl ether and bis(triphenylphosphine)-iminium chloride, PPNCl, was recrystallized from acetone–hexane. The TBAP was vacuum dried for a minimum of 48 h prior to use.

(ii) Electrochemical experiments

All electrochemical experiments were done under a blanket of nitrogen or argon. Conventional cyclic voltammetry was done with EG&G 362 and BAS CV 27 potentiostats in a three-electrode configuration. The working electrode was a platinum disk (1.6 mm in diameter) and the counterelectrode was a platinum wire. The reference was a Metrohm Ag/AgCl electrode filled with a mixture of dichloromethane and 0.1 M TBAP and saturated with LiCl; this was separated from the test solution by a salt bridge containing dichloromethane or butyronitrile and 0.1 M TBAP.

Platinum disk microelectrodes of radii 25 and 50 μm were fabricated by sealing the microwire in soda glass as previously described [14]. Smaller microelectrodes down to a radius of 0.5 μm were made according to a recently published procedure [15]. Fast scan voltammetry with microelectrodes (50–5000 V s^{-1}) was performed using a two-electrode arrangement. The voltage ramp was supplied by an EG&G Model 175 Universal Programmer. The current was measured with a homemade *I/E* converter based on an OP-37 operational amplifier. The data were collected by a Gould Model 4035 digital oscilloscope and transferred to an *X–Y* recorder. A platinum wire pseudoreference electrode was used for all fast scan work in order to minimize the ohmic *iR* drop. Steady state voltammetry with platinum disk microelectrodes was performed in the two-electrode configuration with an Ag/AgCl reference. The electrochemical cell was placed inside a solid aluminum Faraday cage. An EG&G Model 175 provided the voltage ramp and a Keithley Model 427 current amplifier was used to convert current to a voltage signal that was fed to a Nicolet 3091 digital oscilloscope and then to an IBM AT computer for display and analysis by Asystant + software (Macmillan Software Co., New York).

Temperature measurements were made with a Matronics MAT 100 K thermocouple probe inserted into the electrochemical cell. Experiments at low temperature were performed by placing the cell in a slush bath containing dichloromethane, methanol, ethanol, or butyronitrile. In order to obtain the low temperature voltammogram of the thermally unstable complex Fe(TPP)(MeIm)Cl, a solution of Fe(TPP)Cl in dichloromethane was cooled to ca. $-90\,^{\circ}$C and sufficient MeIm added via a gas-tight syringe to produce a ca. 0.05 M MeIm solution; the product Fe(TPP)(MeIm)Cl forms rapidly and is stable at $-90\,^{\circ}$C. Conductivity measurements in butyronitrile showed that Fe(PPDME)Cl is unionized relative to PPNCl.

C. RESULTS AND DISCUSSION

(i) Variable-temperature voltammetry

While there have been a number of published studies involving voltammetric experiments at temperatures higher or lower than ambient, most inorganic chemists who utilize electrochemical techniques do not routinely vary the temperature. As shown by the example below, voltammetric measurements at high or low temperatures are usually simple to perform and can be mechanistically very informative. Low temperature cyclic voltammetry (LTCV) has been mostly confined to protic or polar aprotic solvents (methanol, dimethylformamide (DMF), butyronitrile) [16,17]. It is less well known that LTCV is easily done in relatively nonpolar media such as dichloromethane, which can be quite useful because reactive molecules are often more persistent in such solvents than in more polar ones [18–22]. By varying the temperature, rate and equilibrium constants change, and advantage of this may be taken to identify and characterize reaction mechanisms. LTCV is particularly useful in this regard, and in this paper examples are given showing how it may be used to (1) study thermally unstable species prepared chemically at low temperature, (2) detect transients produced electrochemically, and (3) convert chemically irreversible waves into reversible ones and vice versa. In a related manner, reversible charge transfer can be converted to irreversible behavior by lowering the temperature.

Butyronitrile is an excellent solvent for variable-temperature studies because of its wide potential window, large dielectric constant (20.3), good solvating properties for electrolytes and most substrates, and wide liquid range (117 to $-112\,^{\circ}$C). A good example of the utility of this solvent is provided by a recent LTCV study [17] of dibromoalkanes at temperatures down to $-120\,^{\circ}$C. On the high temperature side, Fig. 1 shows the CV of Fe(PPDME)Cl in butyronitrile at $100\,^{\circ}$C. On the basis of published studies [20,22–24] of various Fe(porphyrin)Cl complexes, it is fairly certain that the mechanism in Scheme 1 obtains, where Fe denotes the Fe(porphyrin)

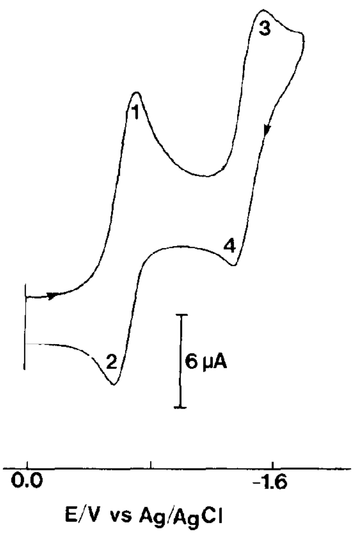
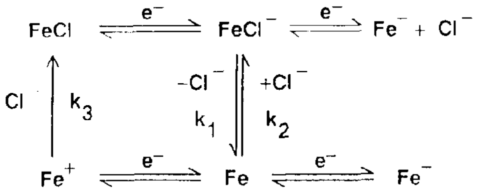


Fig. 1. Cyclic voltammogram of 1.0×10^{-3} M Fe(PPDME)Cl in butyronitrile (0.1 M TBAP) at 100 °C. The working electrode was a platinum disk 1.6 mm in diameter and the scan rate was 300 mV s^{-1}.



Scheme 1.

moiety. It is implicit that the solvent and the electrolyte anion (ClO_4^-) are available for coordination, especially to Fe and Fe^+. FeCl is reduced at wave 1 (Fig. 1) and the $FeCl^-$ product rapidly dissociates, losing chloride ion to give Fe, which is reduced to Fe^- at wave 3. On the reverse scan, Fe^- is oxidized to Fe (wave 4) and at wave 2 oxidation back to FeCl via $FeCl^-$ occurs; the direct oxidation of Fe to Fe^+ is not seen (except at low temperatures or fast scan rates) because both k_1 and k_2 are large, so that Fe and $FeCl^-$ are in equilibrium. The order of reduction potentials in Scheme 1 is deduced to be $E(Fe^+) > E(FeCl) > E(Fe) > E(FeCl^-)$.

By using rapid scan rates with microelectrodes (vide infra) and by lowering the temperature, some of the details of the mechanism in Scheme 1

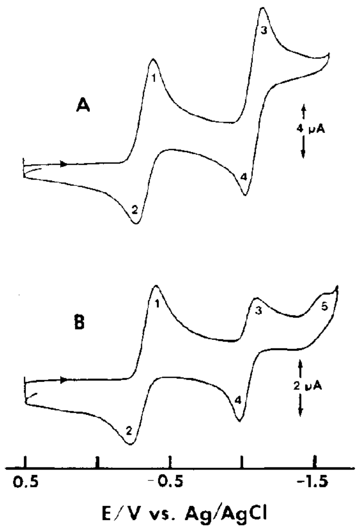


Fig. 2. Cyclic voltammogram of 9.9×10^{-4} M Fe(TPP)Cl in dichloromethane (0.1 M TBAP) at (A) 16 °C and (B) −85 °C. The working electrode was a platinum disk 1.6 mm in diameter and the scan rate was 300 mV s^{-1}. (Reprinted with permission from ref. 20. Copyright 1986 Elsevier Sequoia S.A.)

can be elaborated. Some low temperature results are given in Figs. 2 and 3. The solvent for these LTCV experiments was dichloromethane and Figs. 2 and 3 serve to illustrate that high quality CVs are readily obtained at −90 °C in this relatively nonpolar solvent. (For FeCl complexes, LTCV in butyronitrile gives qualitatively similar results.) Looking first at Fig. 2, the most obvious effect of temperature is a decrease in the peak current ratio for waves 3 and 1 [20]. Thus the ratio for wave 3/wave 1 is unity at 16 °C and falls to 0.4 at −85 °C at 300 mV s^{-1}. The low temperature ratio is independent of porphyrin concentration but decreases markedly with increasing scan rate. Figure 3 shows that the dependence of the wave 3/wave 1 current ratio on temperature is even more marked with Fe(TPP)N_3 [22]. Indeed, at −90 °C the wave 3/wave 4 couple virtually disappears. Within the context of Scheme 1 the obvious interpretation of these observations is that at low temperature, chloride (or azide) dissociation from FeX^- ($X^- = Cl^-, N_3^-$) is slowed down so that conversion to Fe + X^- is incomplete on the CV time scale, with a consequent decrease in the current for the wave 3/wave 4 couple. The current ratio for wave 3/wave 1 is concentration independent because the dissociation step is first order, but it does depend on scan rate since this defines the time available for dissociation. The LTCV data show that the rate constant (k_1) for X^- dissociation from FeX^- is

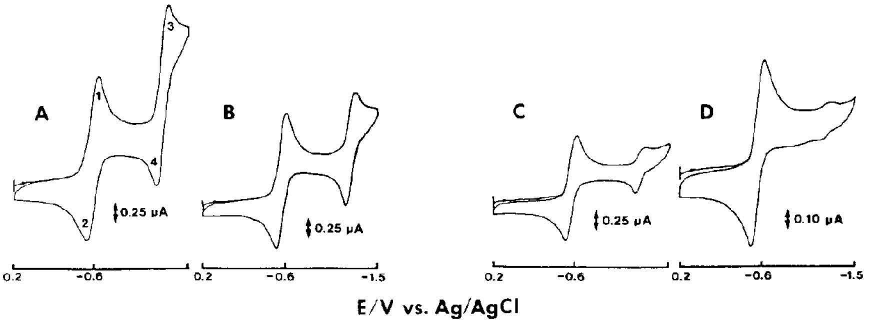
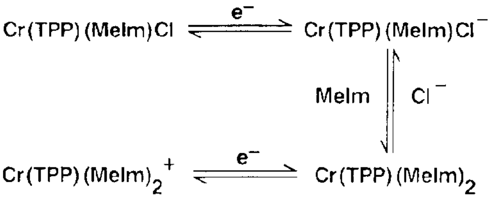


Fig. 3. Cyclic voltammograms of ca. 10^{-4} M $Fe(TPP)N_3$ in dichloromethane (0.1 M TBAP) at (A) 20 °C, (B) −45 °C, (C) −70 °C and (D) −90 °C. The working electrode was a platinum disk 1.6 mm in diameter and the scan rate was 100 mV s^{-1}. (Reprinted with permission from ref. 22. Copyright 1986 American Chemical Society.)

much smaller for $X^- = N_3^-$ than for $X^- = Cl^-$; on the basis of relative basicities and kinetic studies of Fe(porphyrin)X complexes [22,25], this is the expected result.

If dissociation of X^- from FeX^- is incomplete at low temperature, a new wave might be expected to appear for the reduction of FeX^-. Wave 5 in Fig. 2B is assigned in this manner. A similar process could not be detected with $Fe(TPP)N_3$ owing to interfering porphyrin ring reductions.

Figure 4 illustrates a complicated system that is greatly simplified by LTCV, and Scheme 2 summarizes the chemistry involved [19]. The reaction mixture contains Cr(TPP)(MeIm)Cl in the presence of excess MeIm and Cl^-. At room temperature, Cr(TPP)(MeIm)Cl reduction gives the chemically irreversible wave 1. Rapid chloride dissociation produces $Cr(TPP)(MeIm)_2$ which is oxidized at wave 2, and the $Cr(TPP)(MeIm)_2^+$ so formed that remains at the electrode surface is reduced at wave 3. At −10 °C the chloride dissociation from $Cr(TPP)(MeIm)Cl^-$ is slow enough so that partial chemical reversibility is present (wave 4). At −91 °C the chloride dissociation is very slow so that only the wave 1/wave 4 couple remains.



Scheme 2.

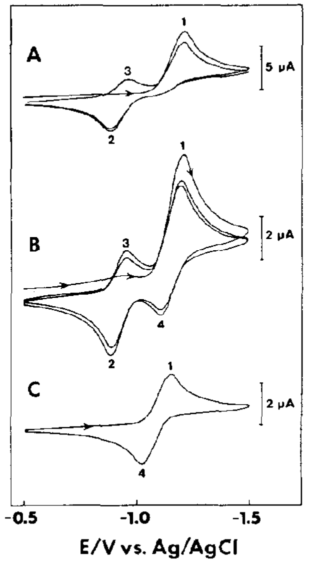


Fig. 4. Cyclic voltammogram of 7.3×10^{-4} M Cr(TPP)(MeIm)Cl in dichloromethane with 0.06 M MeIm present. The temperatures were (A) 20 °C, (B) −10 °C and (C) −91 °C and were recorded in the sequence A, C, B. The supporting electrolyte was 0.1 M TBACl, the working electrode a platinum disk 1.6 mm in diameter, and the scan rate 200 mV s^{-1}. (Reprinted with permission from ref. 19. Copyright 1986 Royal Society of Chemistry.)

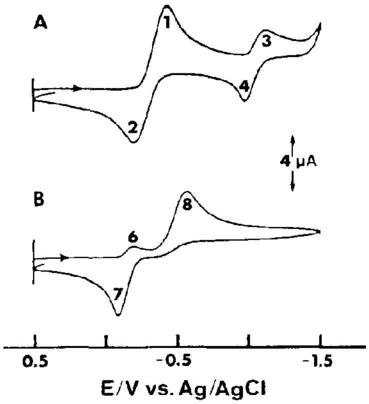


Fig. 5. Cyclic voltammogram of 2.0×10^{-3} M Fe(TPP)Cl in dichloromethane (0.1 M TBAP) at (A) −88 °C and (B) −87 °C with 0.04 M MeIm present. The working electrode was a platinum disk 1.6 mm in diameter and the scan rate was 300 mV s^{-1}. (Reprinted with permission from ref. 20. Copyright 1986 Elsevier Sequoia S.A.)

The most important use of LTCV is in the study of reactive chemical species prepared at low temperatures, and an example of this is illustrated in Figs. 5 and 6 [20]. Looking first at Fig. 5, it can be seen that the addition of MeIm to Fe(TPP)Cl at −88 °C leads to a dramatic change in the CV. It is known from extensive kinetic and spectroscopic studies that Fe(TPP)Cl reacts cleanly and completely to give the six-coordinate complex Fe(TPP)(MeIm)Cl which has a half-life of only 10 ms at room temperature, but which is stable in dichloromethane below ca. −90 °C. Wave 8 in Fig. 5B is due to the chemically irreversible reduction of this complex to give Fe(TPP)(MeIm)Cl$^-$, which rapidly loses chloride to form Fe(TPP)(MeIm)$_2$. The latter complex is oxidized at wave 7; wave 6 present on the initial negative scan is due to a small amount of Fe(TPP)(MeIm)$_2^+$ that forms thermally in the bulk solution. Figure 6 shows the use of LTCV to follow the thermal conversion in the bulk of the reactive Fe(TPP)(MeIm)Cl to the thermodynamic product, Fe(TPP)(MeIm)$_2^+$. It should be noted that the kind of study summarized in Figs. 5 and 6 is only possible by using low temperature techniques.

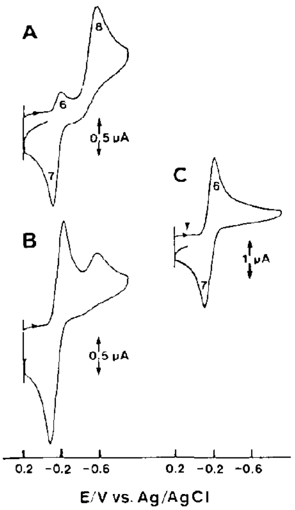


Fig. 6. Cyclic voltammograms of 6.0×10^{-4} M Fe(TPP)Cl and 0.05 M MeIm in dichloromethane (0.1 M TBAP) at (A) −90 °C, (B) −82 °C and (C) −69 °C. The CVs were recorded in the sequence A, B, C at intervals of 5 min. The working electrode was a platinum disk 1.6 mm in diameter and the scan rate was 300 mV s^{-1}. (Reprinted with permission from ref. 20. Copyright 1986 Elsevier Sequoia S.A.)

(ii) Microelectrode voltammetry

At fast sweep rates, microelectrodes display the same current response seen at conventional electrodes with the important differences that the *iR* distortion is diminished and the response time for charging the double layer (*RC* time constant) is faster. This has the important consequence that much faster sweep rates are possible at microelectrodes, e.g. nearly 10^6 V s^{-1} at a platinum disk electrode of radius 5 μm have recently been reported [7]. Such rapid scan rates permit the detection of chemical reactions in the time range of ca. 10 ns, and has recently been used to measure a second-order rate constant of 10^9 M^{-1} s^{-1} for the dimerization of an electrochemically generated organic radical anion [7]. Thus microelectrodes allow the observation of electrogenerated intermediates that react in a bimolecular manner with a rate constant approaching the encounter-controlled limit. Fast sweep CV with microelectrodes may also be used to measure large heterogeneous charge transfer rate constants (greater than 1 cm s^{-1}) which cannot be

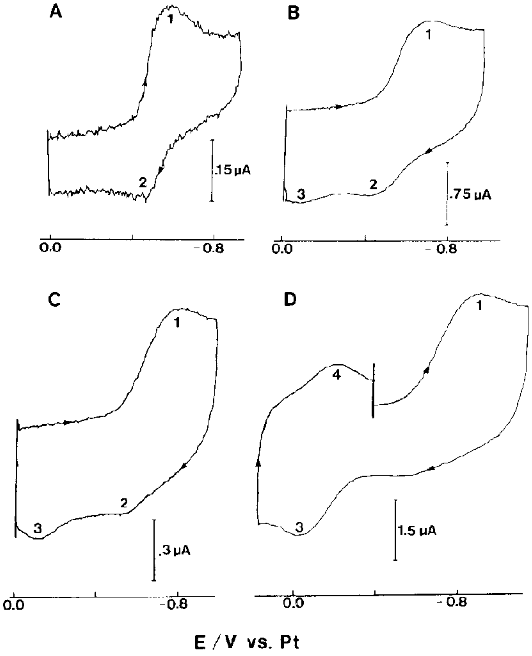


Fig. 7. Cyclic voltammogram of 1.0×10^{-3} M Fe(PPDME)Cl in butyronitrile (0.5 M TBAP) at 20 ° C. The scan rates and the platinum disk working electrode radii were (A) 50 V s^{-1}, 50 μm, (B) 500 V s^{-1}, 50 μm, (C) 1000 V s^{-1}, 25 μm, (D) 5000 V s^{-1}, 25 μm.

measured with conventional electrodes because of the restriction to much lower sweep rates.

Figure 7 shows fast sweep CVs of Fe(PPDME)Cl in butyronitrile with a two-electrode configuration. It should be noted that in spite of the lack of potentiostatic control, *iR* distortion, though evident, is not a major problem. In Fig. 7 the CVs at 50 and 500 V s^{-1} were obtained with a microelectrode of radius 50μm and those at 1000 and 5000 V s^{-1} with an electrode of radius 25 μm. In contrast to what might be normally anticipated, the noise level or signal-to-noise ratio improves as the sweep rate increases. This illustrates a general consideration when using microelectrodes. At fast sweep rates the currents are reasonably large because the small electrode area is compensated for by the square root dependence of current on sweep rate; this means that a smaller microelectrode, which gives less distortion, can be used as the sweep rate increases. At relatively slower sweep rates the inherently small currents are plagued by more noise and hence a larger microelectrode or different instrumental configuration is required.

Inspection of Fig. 7 shows that wave 2 decreases and wave 3 increases in prominence as the sweep rate increases. Within the context of Scheme 1 the interpretation is fairly straightforward. On the positive scan the oxidation can occur via $FeCl^-$ or, at a more positive potential, via Fe. As the sweep rate increases, more of the oxidation occurs through Fe because the second-order rate constant k_2 is not large enough to permit complete conversion to $FeCl^-$. (Analogous behavior has been shown to occur with Fe(TPP)Cl in DMF [24].) At 5000 V s^{-1} (Fig. 7D) the time scale is sufficiently short so that conversion of the Fe^+ so formed to FeCl is incomplete, and a wave (4) corresponding to the direct reduction of Fe^+ (probably present as $FeClO_4$) is observed when the scan is continued negative as shown.

While the familiar linear diffusion predominates at a microelectrode with rapid sweep rates, the diffusion field is convergent (approximately spherical) at slow sweep rates [8], which gives rise to a steady state current response (sigmoidal rather than peak shaped) as illustrated by the CV of $Fe(OEP)(MeIm)_2^+$ shown in Fig. 8 at a microelectrode of radius 0.5 μm and with a scan rate of 20 mV s^{-1}. The change-over from a time-dependent (cottrellian) to a steady state response as a function of decreasing sweep rate occurs gradually. The sweep rate necessary for predominantly steady state behavior is a strong function of the electrode size [5,26]. It is possible to obtain a steady state voltammogram at ca. 20 mV s^{-1} and then, with the same electrode and cell arrangement, obtain the cottrellian voltammogram by going to faster sweep rates (e.g. 100 V s^{-1}).

Steady state voltammograms are particularly convenient to record and possess little or no *iR* distortion or charging current contribution. The rate of mass transport to the microelectrode is large under steady state condi-

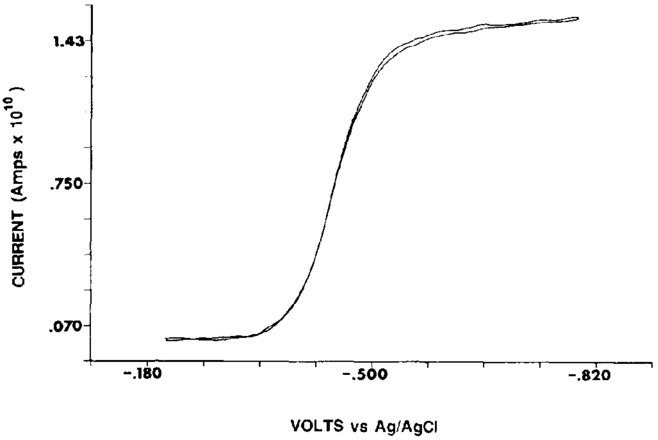


Fig. 8. Cyclic voltammogram of 1.0×10^{-3} M $Fe(OEP)(MeIm)_2^+$ in dichloromethane (0.1 M TBAP) at 25 °C with excess MeIm present at 1.0 M. The working electrode was a platinum disk of radius 0.5 μm and the scan rate was 20 mV s^{-1}; the scan started at −0.20 V. OEP is the dianion of octaethylporphyrin. (Reprinted with permission from ref. 15. Copyright 1988 American Chemical Society.)

tions, with the result that chemical reactions following charge transfer do not affect the voltammogram unless they are very rapid. The sensitivity to homogeneous chemical steps as well as to the kinetics of charge transfer are a strong function of electrode size and so the experiment can be "tuned" to the system being studied by varying the size of the electrode. The limiting diffusion current in the steady state voltammogram is given by the simple expression $i_L = 4nFDCr$, where C is the bulk concentration of the electroactive species. The shape of the entire voltammogram is understood theoretically [8,9] and it is known that parameters such as $E_{1/2}$ and $(E_{1/4} - E_{3/4})$ are a sensitive function of k_s when the charge transfer is not completely reversible. The theoretical expressions for irreversible and quasi-reversible charge transfer at a microdisk electrode are relatively complex. However, treating the disk microelectrode as a hemisphere, which is easily treated theoretically, may be an acceptable approximation for some mechanisms. This, however, has yet to be demonstrated.

The value of $(E_{1/4} - E_{3/4})$ in Fig. 8 for the reduction of $Fe(OEP)(MeIm)_2^+$ is 73 mV, which is significantly greater than the value of 56 mV predicted for reversible charge transfer [8]. From these data it can be shown [9] that the charge transfer rate constant k_s is ca. 0.2 cm s^{-1}, which is significantly larger than the reported value [27] of 0.04 cm s^{-1} determined with a conventional platinum electrode in a solution of the same composition. Similarly, the effect of charge transfer with $Fe(TPP)(MeIm)_2^+$ is shown in

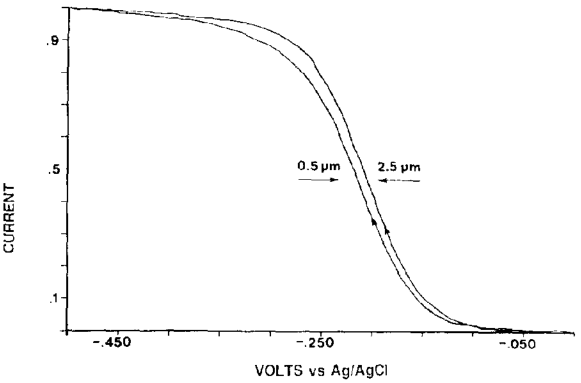


Fig. 9. Linear sweep voltammograms of 1.0×10^{-3} M $Fe(TPP)(MeIm)_2^+$ in dichloromethane (0.1 M TBAP) at 25 °C with excess MeIm present at 1.0 M. The sweep rate was 20 mV s^{-1} and the working electrodes were platinum disks of radii 0.5 and 2.5 μm. The current scale is normalized with 1.0 unit corresponding to 0.13 nA and 0.65 nA for the 0.5 μm and 2.5 μm electrode respectively.

Fig. 9; it should be noted that both $E_{1/2}$ and $(E_{1/4} - E_{3/4})$ depend on electrode size such that the charge transfer is more reversible at the larger electrode. Again the data indicate [9] a k_s significantly larger than previously reported. Steady state microelectrode experiments with ferrocene also indicate a larger k_s than previously claimed and in this case the discrepancy is more than one order of magnitude [5]. It is likely that residual ohmic *iR* distortion present with conventional electrodes accounts for the disagreement with the k_s values determined with microelectrodes.

The information obtainable from steady state and fast scan data with microelectrodes is similar but not identical, and it is recommended that both scan rate regimes be utilized when investigating the heterogeneous electron transfer and/or coupled homogeneous reactions of a given system. With fast scan data the readily accessible planar diffusion theory can be used, but *iR* drop and charging current effects are much less under steady state conditions, giving rise to more accurate measurement. It should be noted that microelectrodes used under steady state conditions have several other advantages not generally available with conventional electrodes. These include the feasibility of doing voltammetric experiments (1) with little or no electrolyte present [28] and (2) in nonpolar solvents like benzene, toluene, and even heptane [29–31].

D. CONCLUSION

The chemistry summarized in this paper illustrates that the voltammetric examination of inorganic redox mechanisms can be significantly facilitated by the use of microelectrode techniques and/or by variable temperatures. Researchers in inorganic, organometallic, and organic chemistry should find both approaches very useful. It is likely that microelectrodes will be routinely utilized by chemists in the near future.

ACKNOWLEDGEMENTS

This work was financially supported by the Australian Research Grants Scheme, the National Science Foundation (CHE-8521189), and the National Institutes of Health (DK-30145). D.A.S. is the recipient of an NIH Research Career Development Award (1983–1988). G.A.T. is grateful to the Australian–American Education Foundation for a Fulbright Fellowship (1987), and to Southern Oregon State College for a leave of absence.

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