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Low Temperature Electrochemistry of Metalloporphyrins in Dichloromethane: Characterization of Transient Species

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Abstract

Cyclic voltammetry in dichloromethane at temperatures down to −90 °C has been used to characterize Fe(TPP)Cl (TPP = tetraphenylporphyrin dianion) and the transient high-spin six-coordinate complex [Fe(TPP)(MeIm)Cl] (MeIm = *N*-methylimidazole). It is shown that low temperature cyclic voltammetry (LTCV) in dichloromethane can give high quality results using standard equipment and electrode systems; IR drop is not a serious problem. At −85 °C the anion $Fe(TPP)Cl^-$ slowly dissociates chloride and separate waves can be seen for the subsequent reduction of $Fe(TPP)Cl^-$ and Fe(TPP); this is not observed at room temperature. In the presence of excess MeIm, the transient species [Fe(TPP)(MeIm)Cl] decays with a half life of *ca.* 10 ms at room temperature, but at −90 °C is sufficiently persistent to allow electrochemical characterization. Its reduction occurs at a potential *ca.* 130 mV negative of that for Fe(TPP)Cl and is chemically irreversible, rapidly converting to $Fe(TPP)(MeIm)_2$. The utility of low temperature electrochemistry for investigating unstable metalloporphyrins in relatively nonpolar solvents is discussed.

Introduction

Metalloporphyrin complexes with a variety of axial ligands have been extensively investigated as models for the chemistry involving heme proteins. Electrochemical studies of metalloporphyrins are especially important since electron transfer to/from the heme moiety plays a primary role in many heme protein mediated reactions. For the most part, the published electrochemical work [1–3] has involved room temperature measurements on stable species. However, it would be quite useful to be able to make measurements at low temperatures (*ca.* −90 °C) in relatively nonpolar solvents (e.g., CH_2Cl_2) because these conditions would allow the study of highly reactive metalloporphyrin species that model heme proteins and their reaction intermediates. A few examples of metalloporphyrins in this category include the following bonding types: iron–dioxygen (Fe(II)–O_2 or Fe(III)–O_2^-) [4–7], iron–peroxide (Fe(III)–O–O–Fe(III)) [8], iron–oxygen atom (Fe(IV)–O^- or Fe(V)–O^{2-}) [8–12], and iron–thiolate (Fe–SR) [13–19]. To this list can be added models with other axial ligands and metals other than iron (especially Co, Ru, Cr, Mn). These or related species are known or believed [20–25] to be important in the chemistry of cytochrome P450, peroxidases (Compounds I, **II**, and **III**), catalases, hemoglobin (autoxidation), etc. Low temperature electrochemistry of these generally unstable model complexes should provide valuable information concerning redox potentials, electrochemical reversibility, electron transfer rates, and the nature of the products of electron transfer (with associated mechanisms). This in turn should be very useful for understanding the catalytic cycles of heme proteins, especially P450 and the peroxidases.

There exist several reports of low temperature electrochemistry of metalloporphyrin complexes in polar solvents. In the most significant of these it was shown [26] that $[Fe(OEP)L(O_2)]$ (OEP = octaethylporphyrin dianion; L = solvent) is reversibly reduced to a peroxo species at −25 °C in MeCN/Me_2SO (1:1 v/v). There is also a report of the reduction of $Fe(TPP)N_3$ (TPP = tetraphenylporphyrin dianion) at −58 °C in DMF [3]. In order to study many transient metalloporphyrins, however, lower temperatures and less polar solvents are required. In this paper we show that electrochemistry on metalloporphyrins can be easily performed at −90 °C in dichloromethane. Furthermore, only standard equipment and electrode systems are needed.

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The utility of low temperature electrochemistry for characterizing metalloporphyrins and other classes of compounds, especially organometallics, is obvious, yet the technique has been rarely applied. Probably a major reason for this is a belief that increased solution resistance and lowered diffusion coefficients would preclude high quality results at low temperatures in relatively nonpolar solvents. With some protic and polar aprotic solvents (e.g., MeOH, DMF, EtCN) electrochemical work at or below –70 °C is known to be possible [27]. The usefulness of dichloromethane under these conditions was reported [27] to be limited due to excessively high resistance. We have shown previously that voltammetry at –75 °C in acetone can be utilized to study reactive organometallic species, e.g., $[Cr(CO)_5X]^+$ (X = halide) [28].

Low temperature electrochemistry, especially low temperature cyclic voltammetry (LTCV), has three useful applications. These are (1) the investigation of thermally unstable species prepared chemically at low temperatures, (2) the detection of transients produced electrochemically, and (3) the conversion of chemically irreversible waves into reversible ones. LTCV in relatively nonpolar media such as dichloromethane is especially attractive because reactive molecules are often more persistent than in more polar media. While these points are rather obvious, the fact is that there are no reports of LTCV in unreactive solvents that clearly demonstrate any of the above three applications. In this paper we illustrate the utility of LTCV with respect to points (1) and (2). For point (2) we chose Fe(TPP)Cl because this complex has been previously studied at room temperature by electrochemical techniques [29–34]. To test point (1), which is the most important application of LTCV, we chose the transient high-spin six-coordinate species [Fe(TPP)(MeIm)Cl] (MeIm = *N*-methylimidazole), which is formed as an intermediate in reaction (1). We have shown [35–38]

$$\mathrm{Fe(TPP)Cl + 2MeIm \longrightarrow Fe(TPP)(MeIm)_2{}^+Cl^-} \qquad (1)$$

that [Fe(TPP)(MeIm)Cl] converts to products with a half life of 10 ms at 25 °C in CH_2Cl_2. However, at *ca.* –80 °C the transient is sufficiently persistent to permit characterization by standard physical methods (optical spectroscopy, ESR, conductivity). Thus, eqn. (1) represents a good system with which to evaluate the utility of low temperature electrochemistry in the metalloporphyrin field.

Experimental

Fe(TPP)Cl was synthesized from $[Fe(TPP)]_2O$ by a standard procedure [39]. The solvent for the electrochemical experiments was reagent grade dichloromethane, which was dried with 4 Å molecular sieves and verified to be free of redox active impurities by cyclic voltammetry. Experiments with Fe(TPP)Cl utilized a standard 15 ml cell with Fe(TPP)Cl in the concentration range 2.6 to 20×10^{-4} M in CH_2Cl_2. The electrolyte was tetrabutylammonium perchlorate (TBAP) at 0.1 M. The working electrode was a platinum disk and the counter electrode was a platinum wire. The reference consisted of a Metrohm Model 6.0724.040 Ag/AgCl electrode in CH_2Cl_2, which was 0.1 M in TBAP and saturated with LiCl. The reference electrode was connected to the cell via a salt bridge containing CH_2Cl_2 with 0.1 M TBAP. Nitrogen saturated with CH_2Cl_2 was bubbled through the solution for ten minutes and then blanketed over the solution during measurements. Most cyclic voltammograms (CVs) were obtained with a BAS CV27 instrument at a scan rate of 300 mV/s and recorded on a Houston X–Y recorder. CVs at faster scan rates were obtained with a BAS 100 system. The probe of a Matronics MAT 100 K thermocouple meter was placed immediately adjacent to the working electrode, which was itself placed very close to the reference electrode. Measurements at low temperatures were obtained by placing the cell in a CH_2Cl_2 slush bath (*ca.* –95 °C); this simple procedure allowed facile attainment of temperatures down to –90 °C with a control of ±2 °C over *ca.* 20 min. At low temperatures some of the TBAP precipitated from solution and, therefore, it is best to describe the solutions as saturated in electrolyte. Sufficient TBAP remained dissolved so that CVs were readily obtainable (*vide infra*).

After recording the CV of Fe(TPP)Cl at *ca.* –90 °C, 0.20 ml of MeIm (2.0 to 4.0 M) in CH_2Cl_2 (with 0.1 M TBAP) was injected into the cell with a Hamilton 1825 gastight syringe. After thorough mixing via N_2 bubbling, the CV was recorded as a function of time and/or temperature. The experiment was repeated twelve times over a four week period and was highly reproducible. Day to day potential changes in the reference electrode were essentially nil as determined by referencing to ferrocene (5×10^{-4} M) at all temperatures utilized.

Results and Discussion

Fe(TPP)Cl

Figure 1 shows the cyclic voltammogram of Fe(TPP)Cl at +16 °C and –85 °C. The most noteworthy aspect of Fig. 1 is the high quality of the low temperature CV in CH_2Cl_2 as the solvent. As expected, the CV at –85 °C shows a smaller current and somewhat greater peak to peak separation. Table I lists numerical data for Fe(TPP)Cl and other compounds studied. Except for oxidation wave 2 in Fig. 1 (*vide infra*), the peak to peak separations were

TABLE I. Electrochemical Data for Porphyrin Complexes[a]

Complex	Temperature (℃)	E_p^{red} (V)[b]	$E_{1/2}$ (separation (mV))[b,c]
Fe(TPP)Cl	20 ± 5	−0.39, −1.14	−0.33(120); −1.09(100)
	−85 ± 5	−0.42, −1.11	−0.32(200); −1.05(110)
$Fe(TPP)(MeIm)_2{}^+Cl^-$	20 ± 5	−0.22	−0.17(90)
	−85 ± 5	−0.21	−0.15(110)
Fe(TPP)(MeIm)Cl	−85 ± 5	−0.55	–

[a] In CH_2Cl_2 with 0.1 M TBAP. Data is average of 12 experiments at a scan rate of 300 mV/s and porphyrin concentration range of 5×10^{-4} to 2×10^{-3} M. [b] $E_{1/2}$ for ferrocene (5×10^{-4} M) at 20 ℃ was +0.46 V (peak separation of 80 mV) and at −85 ℃ was +0.43 V (peak separation of 110 mV). [c] $E_{1/2}$ taken as $(E_p^{red} + E_p^{ox})/2$.

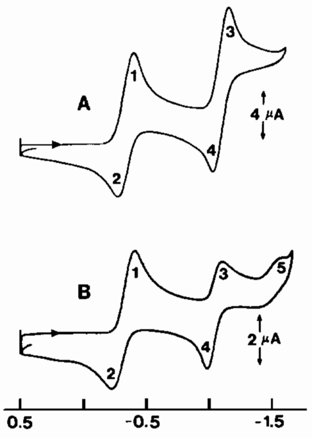

Fig. 1. Cyclic voltammogram of 9.9×10^{-4} M Fe(TPP)Cl in CH_2Cl_2 at (A) + 16 ℃ and (B) −85 ℃. Scan rate 300 mV/s.

in the range 80 to 120 mV at ambient temperature, with the greater separations corresponding to higher concentrations of Fe(TPP)Cl. Ferrocene behaved very similarly, *i.e.*, gave a concentration dependent separation in the range 80 to 130 mV. Accordingly, we attribute the deviation from the 60 mV separation expected for a reversible one-electron change at room temperature to IR drop. This is normal behavior for a solvent as weakly polar as CH_2Cl_2.

The electrochemical behavior of Fe(TPP)Cl in CH_2Cl_2 at room temperature has been previously reported and discussed [29–34] and our results and conclusions are analogous. However, for the sake of comparison with the low temperature results, we now briefly summarize the room temperature behavior. Letting Fe(TPP) be represented as simply Fe, eqns. (2)–(8) can be used to describe the chemistry involved. Explicit consideration may also be given to coordination of perchlorate from the TBAP electrolyte (*vide infra*).

$$FeCl \overset{e^-}{\rightleftharpoons} FeCl^- \qquad (2)$$

$$FeCl^- \rightleftharpoons Fe + Cl^- \qquad (3)$$

$$Fe \overset{-e^-}{\rightleftharpoons} Fe^+ \qquad (4)$$

$$Fe^+ + Cl^- \rightleftharpoons FeCl \qquad (5)$$

$$Fe \overset{e^-}{\rightleftharpoons} Fe^- \qquad (6)$$

$$FeCl^- \overset{e^-}{\rightleftharpoons} FeCl^{2-} \qquad (7)$$

$$FeCl^{2-} \rightleftharpoons Fe^- + Cl^- \qquad (8)$$

Equations (2)–(8) are similar to ones presented elsewhere [3, 32]. With reference to the wave numbering scheme in Fig. 1A, the peak current ratios for 3/4 and 3/1 were found to be close to unity (1.0 ± 0.1) and independent of concentration (2.6 to 20×10^{-4} M) and scan rate (0.10 to 16 V/s). The $E_{1/2}$ for the couple 3/4 was also independent of concentration. The current ratio 1/2 ranged from 1.2 to 2.0 as the concentration decreased or the scan rate increased. As was previously observed [32] with Fe(TPP)Cl in DMF and Fe(TPP)Br in CH_2Cl_2, oxidation wave 2 broadened with increasing scan rate and partially resolved into two oxidation waves at scan rates greater than 1.0 V/s and/or at the lowest concentration used (2.6×10^{-4} M). It is known [3, 34, 40] that $FeCl^-$ readily loses chloride (at room temperature) and that the couple 3/4 refers to eqn. (6). With this information, we conclude that eqn. (3) is rapid in the forward direction and that essentially all chloride is lost from $FeCl^-$. This accounts for the unity peak current ratios for 3/4 and 3/1 and for the invariance of $E_{1/2}$ for 3/4. In spite of this, it can not be concluded that eqn. (3) is in equilibrium, even at the lowest scan rate and highest concentration. This follows because the peak current ratio 1/2 is always greater than unity. Even under the conditions most favoring oxidation via eqn. (2), some oxidation occurs via eqn. (4) at a more positve potential, leading to a broadened oxidation wave 2. Were eqn. (3) in true equilibrium, regardless of the equilibrium constant the peak current ratio 1/2 would be unity and a broadening of the wave 2 would not be observed. More direct evidence for $FeCl^-$ comes from room temperature spectroelectrochemical experiments with Fe(TPP)Cl in dichloroethane [33] and DMF [34], and from cyclic voltammetry in DMF in the presence of a huge excess of chloride ion (1 M) [34].

The electrochemical behavior of Fe(TPP)Cl at −85 °C differs significantly from that at room temperature. The following observations were made (see Fig. 1B and Table I): (1) the peak current ratio for 3/4 is 0.7 ± 0.1 and shows no significant dependence on concentration or scan rate (0.10 to 0.5 V/s); (2) $E_{1/2}$ for the couple 3/4 is concentration independent; (3) the peak current ratio 3/1 is 0.4 ± 0.1 at 300 mV/s and decreases from *ca.* 0.6 to 0.3 over the scan rate range of 0.10 to 1.0 V/s; (4) the current ratio 3/1 is concentration independent; (5) the oxidation wave 2 does not broaden with scan rate (0.10 to 1.0 V/s) nearly as much at room temperature; (6) the peak current ratio 1/2 is 1.4 ± 0.1 at 300 mV/s; (7) a new reduction wave, not present in the room temperature CV, appears at $E_p \approx -1.6$ V (wave 5 in Fig. 1B).

Perhaps the most interesting feature present in the CV of Fe(TPP)Cl at −85 °C that is absent at 16 °C is the appearance of a new wave at *ca.* −1.6 V. We assign this to the direct reduction of $FeCl^-$ (eqn. (7)) which is observed because eqn. (3) is fairly slow in both directions at this temperature. The E_p value of −1.6 V is about what would be expected, *i.e.*, more negative than Fe reduction (eqn. (6)) and similar to that reported [32] for $Fe(TPP)F^-$, which does not dissociate the axial ligand. The reduction wave 5 appears to be chemically irreversible, which is to be expected since the product, $FeCl^{2-}$, should be highly unstable with respect to Fe^- and Cl^- (eqn. (8)). Unfortunately, it is not instructive to scan to potentials much more negative than E_p for 5 because the porphyrin ring is reduced at $E_{1/2} \approx -1.7$ V. (This, of course, also occurs at room temperature.) The sharp inflection at the negative end of wave 5 in Fig. 1B is the onset of ring reduction. The other results listed above for the CV of Fe(TPP)Cl at −85 °C strongly support our conclusion that the equilibration in eqn. (3) is slow enough that separate waves can be seen for the reduction of $FeCl^-$ and Fe. The large reduction of the peak current ratio 3/1 at −85 °C (points (3) and (4)) compared to +16 °C occurs because the forward step in eqn. (3), which begins as soon as FeCl is reduced, is slow at 300 mV/s. About 40% of the $FeCl^-$ has dissociated by the time −1.1 V is reached. As expected, this value depends on scan rate, but does not depend on porphyrin concentration (2.6 to 20×10^{-4} M) because the forward step in eqn. (3) is first order in $FeCl^-$, *i.e.*, the half life is concentration independent. It is important to appreciate that the observation of separate reduction waves for Fe and $FeCl^-$ (3 and 5) is proof that eqn. (3) is not in equilibrium with respect to the time scale of the experiments at −85 °C. When the potential was scanned negative enough to directly reduce $FeCl^-$, the current ratio (3 + 5)/1 was computed as 0.8 ± 0.1. This value is less than unity because between waves 3 and 5 some of the $FeCl^-$ dissociates via eqn. (3) and is immediately reduced to Fe^-.

Points (1) and (2) dealing with the peak current ratio 3/4 at −85 °C can be readily understood. The current ratio is significantly less than unity even when the cathodic potential limits is as positive as −1.4 V, *i.e.*, too positive for the direct reduction of $FeCl^-$. This happens because $FeCl^-$ continues to dissociate after the peak potential for Fe is reached (−1.1 V) and by the time oxidation of Fe^- to Fe (wave 4) is reached, the concentration of Fe^- is amplified accordingly. Since the dissociation of $FeCl^-$ is first order, the 'extra' Fe^- generated by the continuous dissociation of $FeCl^-$ (and reduction of Fe so formed) is such that the ratio 3/4 should be concentration independent, as observed. The dependence of the ratio on scan rate is calculated to be relatively weak over the scan rate range available, and is within the error limit of ±0.1. In principle, the current ratio 3/4 should depend on the cathodic switching potential; in practice the limits utilized were too restricted to permit this to be tested. Additional support for our interpretation can be seen in the shape of wave 3 (see Figs. 1B and 2A). The current after the maximum decays less strongly than that expected from simple diffusion ($t^{-1/2}$) because Fe is continuously generated via eqn. (3).

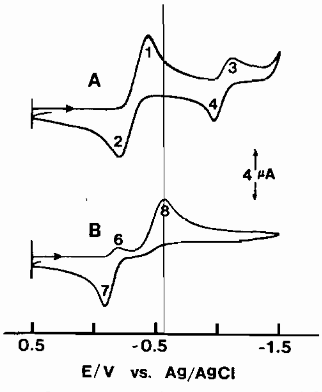

Fig. 2. Cyclic voltammogram of 2.0×10^{-3} M Fe(TPP)Cl in CH_2Cl_2 at (A) −88 °C and (B) −87 °C with 0.04 M MeIm. Scan rate = 300 mV/s.

Finally, it is necessary to consider the behavior of oxidation wave 2, points (5) and (6). As noted above, at +16 °C wave 2 broadened with scan rate due to the slowness of the reverse of eqn. (3). One would expect a more marked effect at −85 °C, but this was not observed; wave 2 did not broaden as at +16 °C and the current ratio 1/2 did not increase with scan rate (0.10 to 1.0 V/s). We suggest that these apparently conflicting observations can be rationalized by considering a refinement of eqns. (2)–(8). At *ca.* −85 °C the association of ligands with Fe will be much greater than at room temperature. In particular, the interaction of electrolyte anion (ClO_4^-) must be more important for eqns. (4) and

$$Fe + ClO_4^- \rightleftharpoons FeClO_4^- \tag{9}$$

$$Fe^+ + ClO_4^- \rightleftharpoons FeClO_4 \tag{10}$$

$$FeClO_4 + Cl^- \rightleftharpoons FeCl + ClO_4^- \tag{11}$$

(5). This is explicitly shown in eqns. (9)–(11). The high perchlorate concentration and enhanced iron-axial ligand interaction (at −85 °C) would shift $E_{1/2}$ for eqn. (4) to a more negative potential, accounting for the failure of wave 2 to split into two separate waves at fast scan rates (in contrast to the behavior at +16 °C). Although the oxidation of Fe at −85 °C may occur directly as $FeClO_4^-$, this is unlikely because a corresponding cathodic shift in wave 3 is not seen. We suggest that eqn. (10) (followed by eqn. (11)) is more dominant at low temperatures and accounts for the apparent cathodic shift in E_p for the oxidation of Fe.

[Fe(TPP)(MeIm)Cl]

The most important application of LTCV is the study of thermally unstable species prepared chemically at low temperatures (*vide supra*). This is illustrated in Fig. 2B, which shows the LTCV obtained after the addition of MeIm (0.03 to 0.05 M) to Fe(TPP)Cl at *ca.* −90 °C. These experimental conditions are known [35–38] to produce the intermediate [Fe(TPP)(MeIm)Cl], which persists for *ca.* 30 min provided the low temperature is maintained. The CV obtained within 2 min of MeIm addition (Fig. 2B) showed three waves. Those labelled 6 and 7 are due to the redox process in eqn. (12). Fe(TPP)-

$$Fe(TPP)(MeIm)_2^+ \overset{e^-}{\rightleftharpoons} Fe(TPP)(MeIm)_2 \tag{12}$$

$(MeIm)_2^+$ is the thermodynamic product and grows in concentration with time or temperature as shown in Fig. 3 (*vide infra*). The wave labelled 8 is assigned to the kinetic intermediate which undergoes a chemically irreversible reduction according to eqn. (13).

$$Fe(TPP)(MeIm)Cl \xrightarrow[MeIm]{e^-} Fe(TPP)(MeIm)_2 \tag{13}$$

It is fully expected that $[Fe(TPP)(MeIm)Cl]^-$ would rapidly dissociate chloride and be trapped by excess MeIm, since the same process occurs with [Fe(TPP)-(MeIm)Cl], albeit more slowly. Eqn. (13) accounts

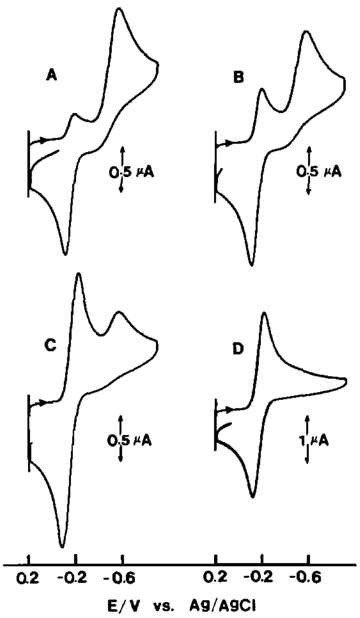

Fig. 3. Cyclic voltammogram of 6.0 × 10^{-4} M Fe(TPP)Cl and 0.05 M MeIm in CH_2Cl_2 at (A) −90 °C, (B) −89 °C, (C) −82 °C, and (D) −69 °C. The CVs were recorded in the sequence A, B, C, D at five minute intervals. Scan rate = 300 mV/s.

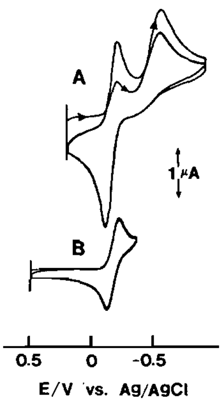

Fig. 4. Cyclic voltammograms of 8.4 × 10^{-4} M Fe(TPP)Cl and 0.03 M MeIm at −87 °C. Initial and subsequent scans are shown with the switching potential (A) negative and (B) positive of the value required to reduce the transient [Fe-(TPP)(MeIm)Cl]. Scan rate = 300 mV/s.

for the greatly enhanced current for wave 7 relative to 6 during the first scan. In subsequent scans the current for 6 is increased and that for 8 decreased appropriately as shown in Fig. 4A. Proof of this interpretation is provided in Fig. 4B, which shows that the current ratio 6/7 is unity when the scan is switched at a potential positive of wave 8. Figure 3 shows that the relative heights of waves 6 and 8 are coupled, with 8 decreasing with temperature and time. At −69 °C all porphyrin exists as Fe(TPP)-$(MeIm)_2^+$; recooling to −90 °C does not regenerate wave 8. The current ratio (6 + 8)/7 remained near unity (1.1 ± 0.1) for all CVs regardless of the relative heights of 6 and 8.

The data show that reduction of [Fe(TPP)(MeIm)-Cl] occurs about 130 mV negative of Fe(TPP)Cl. This is expected since the addition of the ligand MeIm must increase the electron density around the metal and make its reduction more difficult. Actually, the 130 mV shift is probably too small because the chemical irreversible nature of eqn. (13) causes a positive potential shift from the reversible value. That 130 mV is too small cannot be stated with certainty, however, because the reduction of [Fe(TPP)(MeIm)Cl] may not be fully electrochemically reversible and this would lead to a negative potential shift.

The LTCV experiments were repeated using a platinum wire as the reference electrode. While this gave results analogous to those obtained with the Ag/AgCl reference, it offered no advantage and possesses the distinct disadvantage of having a less reproducible electrode potential.

Conclusions

We have shown that electrochemistry at temperatures as low as −90 °C in CH_2Cl_2 presents no difficulties and should be very useful in the study of metalloporphyrins (and other molecules). The present study of reaction (1) via LTCV highlights the kind of information to be gleaned from such investigations. For example, the low temperature results made it possible to show that $Fe(TPP)Cl^-$ dissociates chloride in a relatively slow process and this permitted the direct observation of $Fe(TPP)Cl^-$ reduction. In a related manner, species reactive at ambient temperature can be stabilized and studied at low temperatures, and this was demonstrated with the highly reactive complex [Fe(TPP)(MeIm)Cl]. Applications of this type of research to other porphyrin intermediates (see Introduction) promises to be very fruitful. We also expect that low temperature electrochemistry in nonpolar solvents (e.g., toluene) without supporting electrolyte should be possible using microelectrode technology [41, 42]. We are currently exploring these and other techniques as applied to the low temperature characterization of metalloporphyrins and organometallics.

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