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Electrochemical studies of metal carbonyl compounds

Alan M. Bond, Ray Colton

Department of Chemistry, Monash University, Clayton, Vic. 3168, Australia

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Abstract

This article reviews our studies over some twenty years on the oxidative redox chemistry of 18e carbonyl derivatives of the group 6 and 7 transition metals. The necessity of coupling electrochemical and spectroscopic techniques is emphasized. Probably in all cases, the first oxidative step is a one-electron process and the subsequent chemistry of the system depends upon the stability and reactivity of 17e product. Isomerization is a common phenomenon, but when this is not possible disproportionation is often observed. © 1997 Elsevier Science S.A.

1. Introduction

This article is an overview of our studies over more than twenty years of the redox properties of metal carbonyl compounds. Almost all the electrochemical

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Abbreviations: dpm, $Ph_2PCH_2PPh_2$; dam, $Ph_2AsCH_2AsPh_2$; dpe, $Ph_2PCH_2CH_2PPh_2$; ape, $Ph_2PCH_2CH_2AsPh_2$; dpmS, $Ph_2P(S)CH_2PPh_2$; dpmSe, $Ph_2P(Se)CH_2PPh_2$; apeS, $Ph_2P(S)CH_2CH_2AsPh_2$; apeSe, $Ph_2P(Se)CH_2CH_2AsPh_2$; P₂P', $Ph_2PCH_2CH_2P(Ph)CH_2CH_2PPh_2$

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studies on the normally eighteen electron starting compounds have been oxidative, so a large proportion of our work has been concerned with the formation and subsequent chemistry of paramagnetic seventeen electron species. Although electrochemical studies are the main theme of this review, these techniques alone would not have been sufficient to elucidate the chemistries of many of the systems studied and we have always advocated the application of as many techniques as possible to any system.

Over the 20 year timescale of these studies, the range of electrochemical and other techniques available to us has expanded dramatically, and an exciting part of the challenge of modern chemistry is to make full use of the latest experimental methods which often provide new insights on familiar systems. Thus, we find that some systems, for example $M(CO)_2(dpe)_2$ (M = Cr, Mo, W), have been investigated several times as new techniques have evolved. It is worth noting the progression of techniques over the last twenty years. The earliest cyclic voltammetric measurements were made at what are now referred to as macro disk electrodes (radius 2–5 mm) at scan rates up to only 500 mV s^{-1}; fortunately some of the isomerization reactions of seventeen electron species are of the rate required to be observed under these conditions. The introduction of microelectrodes (e.g. disks of radius 0.5–50 μm [1]) allowed the use of very fast scan rates (e.g. up to 1 000 000 V s^{-1}) and also facilitated steady-state observations, both of which effectively reduce the observable timescales to the millisecond (or less) time domain and therefore enable electrochemical detection of very short-lived intermediates [2,3]. At the same time, the emergence [4,5] of powerful digital simulation techniques for theoretical characterization of postulated electrochemical pa[illegible] has been invaluable. Since metal carbonyl compounds are generally insoluble [illegible]ter, almost all our studies have been made in organic solvents. The range of [illegible]cessible solvents has gradually increased as techniques improved so that with [illegible]roelectrodes it is now possible to use low dielectric media such as benzene and to[illegible] with supporting electrolytes such as tetrahexylammonium salts [1], or solven[illegible] as acetonitrile without any added electrolyte [1,6]. A more recent advance [illegible]n the development of techniques to investigate the electrochemistry of in[illegible] species. These have been used to study the electrochemical behaviour of [illegible]ter insoluble metal carbonyl compounds attached to macroelectrodes when placed in aqueous (electrolyte) media.

In our earliest studies, the major non-electrochemical techniques used to characterize the redox chemistry were IR, ^1H NMR and ESR spectroscopies on isolated samples. Since all 17e species are paramagnetic, ESR measurements have been commonplace in our work. Cells were developed to allow electrolyses within the cavity of the ESR instrument to monitor transient paramagnetic species [7,8] and later still Fourier transform IR (FTIR) techniques allowed observation of low concentrations of carbonyl species in solution or precipitated onto the electrode during electrolysis. The advent of Fourier transform multinuclear magnetic resonance in the 1980s had a major impact on our work as it enabled us to determine the isomeric identity of most species quite unambiguously. We also attempted to find correlations between NMR parameters ($\delta^{13}C$ and $\delta^{31}P$) and E^0 values for an extensive range of $Cr(CO)_5L$ complexes (L = monodentate ligand) [9]. In the last five years we have used electrospray mass spectrometry (ESMS) extensively, including some applications to carbonyl systems [10,11].

Electrochemical sign conventions have had a troubled history and the recommended conventions have changed even within the last twenty years. In this review we will adopt the presently accepted IUPAC convention and as a result some of the diagrams from our earlier papers have been redrawn. We would also like to take this opportunity to recommend in the strongest possible terms that all measurements be referenced against the reversible ferrocene couple (Fc^+/Fc) (internal or external) or some similar standard substance, even though actual measurements may be made against other reference electrodes [12,13]. No one would contemplate recording an NMR spectrum without comparison to the frequency of a reference compound, but the variations between different NMR measurements are trivial compared with the variations in potential which routinely occur in electrochemical studies, even with electrodes that are nominally of the same type. When the often large effects of different junction potentials and different electrolytes in reference electrodes etc. are also appreciated it becomes imperative to use an actually measured standard redox couple as a reference.

The earliest electrochemical studies on metal carbonyl derivatives were invariably reductive and the favoured technique was polarography, which utilises a dropping mercury electrode. In general, the observed responses were two-electron irreversible processes in which a formally two-electron donating ligand was lost so that both the starting material and the product were 18e species. A typical example would be

$$Mo(CO)_6 + 2e^- \rightarrow [Mo(CO)_5]^{2-} + CO$$

and of course this anion can be generated using chemical reductants. Thermodynamic data are only readily extracted from electrochemically reversible processes, so that compounds with the above type of electrochemical process cannot be completely characterized in a theoretical sense unless the process can be slowed sufficiently relative to the electrochemical time scale. This would allow measurements to be made of the unstable intermediates which undoubtedly exist in these seemingly simple electrochemical reductions. At the time we began our investigations there were very few techniques available to us which would allow detailed investigation of mechanistically complex irreversible processes.

Twenty years ago a few stable 17e carbonyl species were known, perhaps the best examples would have been $V(CO)_6$ [14] and *trans*-$[Mo(CO)_2(dpe)_2]^+$ [15]. Thus, there was already the suggestion that at least some 17e carbonyl species are stable and that oxidative studies of metal carbonyl compounds might be rewarding. The timing to commence our studies also was opportune as the first of the modern versatile electrochemical systems such as the Princeton Applied Research (PAR) Model 170 instrument were then commercially available. It is now a matter of history that almost all 18e group 6 and 7 carbonyl compounds, which have been our main areas of interest, may be oxidized both chemically and electrochemically.

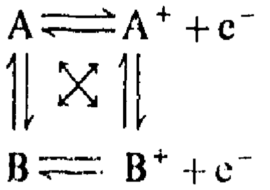
In almost all cases the first step is a one-electron oxidation to the corresponding 17e species and the follow-up chemistry is dependent upon the behaviour of that species. Isomerization of 17e species is commonly observed, but this process can often be effectively prevented by lowering the temperature of the solution upon which the voltammetry is performed. Although low temperature electrochemical measurements on organic systems had been made earlier [16], our studies were the first to use low temperatures to investigate unstable products of metal-based electrochemical reactions. Short timescale microelectrode voltammetry frequently can now provide similar voltammetric information at room temperature, since by using these electrodes the electrochemical timescale "outruns" the kinetic step that occurs after the electron transfer, but low temperatures are still used frequently and often they are essential in bulk electrolysis and spectroelectrochemical experiments.

Although our mandate for this review is to highlight by means of suitable examples some of the more important general themes which have emerged from our work, and to indicate what we believe may be the areas of greatest interest for the next few years, we think it is important to recognise the contributions of others. There have been other much more comprehensive reviews of organometallic redox chemistry [17,18] and there are a number of aspects of carbonyl redox chemistry which we have not pursued, such as redox chemistry in potentially coordinating solvents which leads to extensive substitution chemistry.

Throughout this review oxidative processes will be labelled with a Roman numeral and reductive processes will be given a Roman numeral with a prime superscript. All potentials are quoted versus the reversible couple Fc^+/Fc. A large proportion of the complexes mentioned contain polydentate ligands and if no indication is given of the denticity, then it may be assumed that all donor atoms are coordinated to the metal.

2. The square scheme

The so-called square scheme shown below, describes a sequence of reactions, such as isomerization and cross redox reactions which may accompany the electron



transfer step. However, it is not necessary for all these pathways to be important in particular systems. One of the earliest square schemes we investigated involved the oxidation of *fac*-$Mn(CO)_3(dpm)X$ ($X=Cl$, Br) [19] and it displays many of the features typical of such systems. Fig. 1 shows a cyclic voltammogram at a platinum macroelectrode at 22 °C for the oxidation of an acetonitrile solution (0.1M Et_4NClO_4) of *fac*-$Mn(CO)_3(dpm)Cl$ at a scan rate of $500\ mV\ s^{-1}$. On the first oxidative scan, process I is observed and on the reverse scan there is some, but not complete, reversibility to give process I′ and another reduction process III′ is detected. On the second and subsequent scans processes III, III′ and I, I′ are observed. There

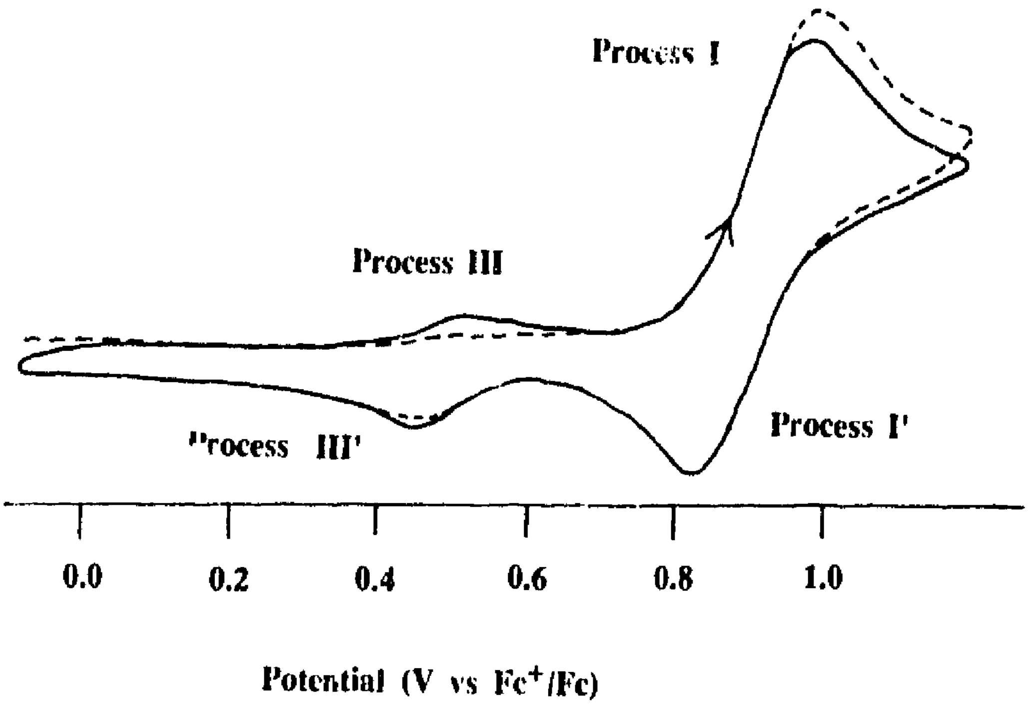


Fig. 1. Oxidative cyclic voltammogram at a Pt disk macroelectrode for the oxidation of *fac*-Mn(CO)$_3$(dpm)Cl in acetonitrile (0.1 M Et$_4$NClO$_4$) at 22 °C, scan rate 500 mV s^{-1}. First scan (- - -), second scan (——) (adapted from Ref. [19]).

is also an additional irreversible oxidative process II at higher positive potential (not shown) which is not relevant to the square scheme. Process II is associated with further oxidation to a 16e species which completely decomposes; similar responses at high positive potential are observed for most carbonyl systems. When the voltammetry is carried out at about −35 °C, redox couple I is completely reversible and process III' does not appear. Thus, the species giving rise to process III' must arise from the product of process I via a kinetic step which is slowed at low temperature. Chemical oxidation of *fac*-Mn(CO)$_3$(dpm)Cl by NOPF$_6$ leads to the isolation of *mer*-[Mn(CO)$_3$(dpm)Cl]$^+$ and its bulk electrochemical reduction gives stable *mer*-Mn(CO)$_3$(dpm)Cl. Both *mer* isomers were identified by analytical and spectroscopic methods (IR, ESR). The isolated *mer* compounds both give only the redox couple III in their cyclic voltammograms. The reaction scheme for the manganese carbonyl system can therefore be written as:

$$\begin{array}{ll} \textit{fac}\text{-Mn(CO)}_3\text{(dpm)Cl} \rightleftharpoons \textit{fac}\text{-[Mn(CO)}_3\text{(dpm)Cl]}^+ + e^- & \text{(couple I)} \\ \qquad\qquad\qquad\qquad\qquad\qquad \downarrow \text{fast} & \\ \textit{mer}\text{-Mn(CO)}_3\text{(dpm)Cl} \rightleftharpoons \textit{mer}\text{-[Mn(CO)}_3\text{(dpm)Cl]}^+ + e^- & \text{(couple III)} \end{array}$$

This simple example of a partial square scheme illustrates several characteristic features of such schemes. The large difference in the reversible $E_{1/2}$ values for the two couples means that the equilibrium position for the reaction

$$\textit{fac}\text{-Mn(CO)}_3\text{(dpm)Cl} + \textit{mer}\text{-[Mn(CO)}_3\text{(dpm)Cl]}^+ \rightleftharpoons$$
$$\textit{fac}\text{-[}e\text{Mn(CO)}_3\text{(dpm)Cl]}^+ + \textit{mer}\text{-Mn(CO)}_3\text{(dpm)Cl}$$

lies almost exclusively to the left and the isolation of *mer*-[Mn(CO)$_3$(dpm)Cl]$^+$ is not therefore surprising. Isolation of *mer*-$\text{Mn(CO)}_3\text{(dpm)Cl}$ appears to be possible only because its isomerization to *fac*-$\text{Mn(CO)}_3\text{(dpm)Cl}$ is kinetically very slow. In contrast, isomerization of *fac*-$[\text{Mn(CO)}_3\text{(dpm)Cl}]^+$ is fast at room temperature.

It turns out that isomerization of the initially produced 17e product is very common and many other examples will be mentioned in this review. It is well known that the electronically preferred stereochemistries of octahedral 18e carbonyl complexes are *cis* for dicarbonyl, *fac* for tricarbonyl and *cis* for bis(ligand)tetracarbonyl compounds. Corresponding *trans* or *mer* geometries are usually observed only if strong steric interactions are present. Thus, in 18e complexes there is competition between electronic and steric preferences in stereochemistry. In view of the common observation of isomerization after oxidation, Mingos [20] undertook a theoretical study of the bonding scheme for 17e species and found that for these species both the electronic and steric preferences were for *trans* and *mer* configurations. The $\mathit{fac}^+ \rightarrow \mathit{mer}^+$ (and $\mathit{cis}^+ \rightarrow \mathit{trans}^+$) isomerization in the 17e configuration is therefore electronically driven and is a fundamental property of these systems.

For those systems in which the 18e species is the sterically preferred isomer, for example *trans*-$\text{Cr(CO)}_4(\text{PPh}_3)_2$, electrochemical or chemical oxidation gives a simple reversible one-electron process giving in this case *trans*-$[\text{Cr(CO)}_4(\text{PPh}_3)_2]^+$. This blue cation can be isolated and it is a useful strong one-electron oxidant [21].

In the particular case of the $\text{Mn(CO)}_3\text{(dpm)X}$ system, the 18e *mer*-$\text{Mn(CO)}_3\text{(dpm)Cl}$ does not isomerize back to *fac*-$\text{Mn(CO)}_3\text{(dpm)Cl}$ at a significant rate, so the cycle of oxidation and subsequent reduction provides a preparative route to the 18e *mer* complex which is not otherwise synthetically accessible. However, in other square schemes the 18e product of reduction may isomerize back to the electronically preferred isomer, for example in the square scheme *trans*-$\text{Mo(CO)}_2(\text{dpe})_2$ rapidly reverts back to *cis*-$\text{Mo(CO)}_2(\text{dpe})_2$ in solution so that only *cis*-$\text{Mo(CO)}_2(\text{dpe})_2$ and *trans*-$[\text{Mo(CO)}_2(\text{dpe})_2]^+$ can be isolated in this system, although all components of the square scheme can be detected voltammetrically at the electrode surface [22]. An unusual feature of this system is that the second oxidation at more positive potential also is reversible at low temperatures, indicating that *trans*-$[\text{Mo(CO)}_2(\text{dpe})_2]^{2+}$ is stable on the voltammetric timescale under these conditions. The corresponding dpm system is similar [23] and both the dpe and dpm complexes *cis*-$\text{M(CO)}_2(\text{P–P})_2$ ($\text{M} = \text{Cr, Mo, W}$; $\text{P–P} = \text{dpm, dpe}$) are readily protonated in acidic media to give stable hydrides $[\text{HM(CO)}_2(\text{P–P})_2]^+$ which have been extensively studied [24,25].

$$\begin{tikzcd}
\mathit{cis}\text{-Mo(CO)}_2(\text{dpe})_2 \arrow[r, leftrightharpoons] & \mathit{cis}\text{-}[\text{Mo(CO)}_2(\text{dpe})_2]^+ + e^- \arrow[d, "\text{fast}"] \\
\mathit{trans}\text{-Mo(CO)}_2(\text{dpe})_2 \arrow[u, "\text{fast}"] \arrow[r, leftrightharpoons] & \mathit{trans}\text{-}[\text{Mo(CO)}_2(\text{dpe})_2]^+ + e^-
\end{tikzcd}$$

The isomeric behaviour of the 18e species produced by the reduction step in the square scheme varies between systems, but in almost all cases the initially produced 17e species isomerizes rapidly, where this is possible geometrically, and the equilibrium position in the 17e configuration strongly favours the isomerized product. The only exceptions we have found to this rule involve either an unusual interplay of electronic and steric forces in complexes of the tridentate ligand P_2P', or where extremely fast cross redox reactions occur following oxidation. Examples of these kinds of systems will be described later in the section dealing with microelectrode experiments.

Occasionally, the initial 17e product of the oxidation isomerizes very quickly and then becomes involved in a cross redox reaction so that a catalytic cycle is established. Fig. 2a shows an oxidative cyclic voltammogram for a dichloromethane (0.1M Bu_4NClO_4) solution of *fac*-$Cr(CO)_3(\eta^1\text{-dpe})(\eta^2\text{-dpe})$ [26]. On the first scan, an

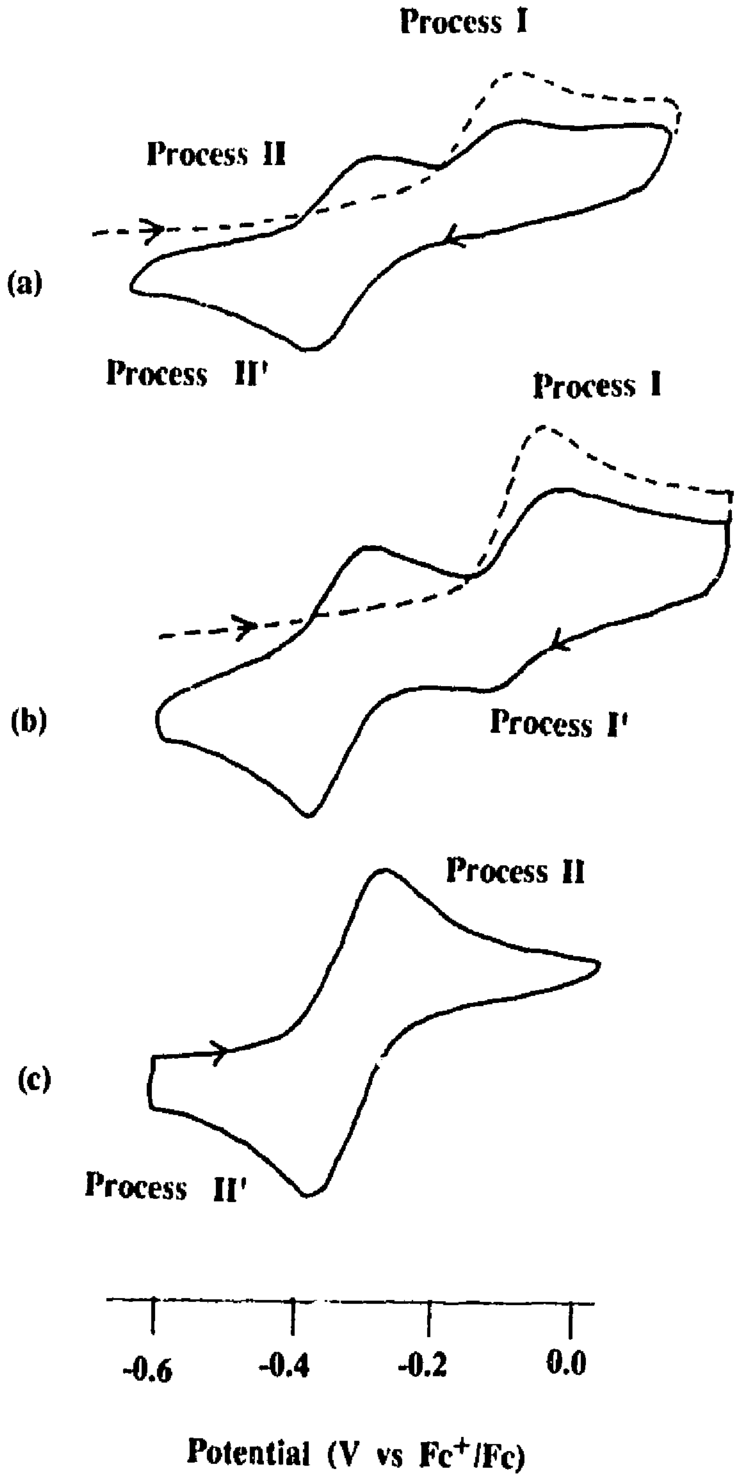


Fig. 2. Oxidative cyclic voltammograms at a Pt disk macroelectrode for the $Cr(CO)_3(\eta^1\text{-dpe})(\eta^2\text{-dpe})$ system in CH_2Cl_2 (0.1M Bu_4NClO_4) at a scan rate of 200 mV s^{-1}. First scans (- - -), second scans (———). (a) Freshly prepared solution of *fac*-$Cr(CO)_3(\eta^1\text{-dpe})(\eta^2\text{-dpe})$ at 20 °C, (b) freshly prepared solution of *fac*-$Cr(CO)_3(\eta^1\text{-dpe})(\eta^2\text{-dpe})$ at −78 °C, (c) the same solution used in (a) about 30 min after the initial cyclic voltammogram at 20 °C (adapted from Ref. [26]).

oxidative process I with a peak potential of −0.070 V is observed but no corresponding reduction is observed on the reverse scan (scan rate 200 mV s^{-1}). However, a reduction wave II′ is observed at −0.370 V and on second and subsequent scans the other half of this couple appears at −0.280 V. Fig. 2b shows a similar cyclic voltammogram at −78 °C for a freshly prepared solution. A small degree of reversibility is now detected for the initial oxidation. In this system the usual reaction

$$\begin{array}{l}
fac\text{-}Cr(CO)_3(\eta^1\text{-dpe})(\eta^2\text{-dpe}) \rightleftharpoons fac\text{-}[Cr(CO)_3(\eta^1\text{-dpe})(\eta^2\text{-dpe})]^+ + e^- \\
\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \downarrow \text{fast} \\
mer\text{-}Cr(CO)_3(\eta^1\text{-dpe})(\eta^2\text{-dpe}) \rightleftharpoons mer\text{-}[Cr(CO)_3(\eta^1\text{-dpe})(\eta^2\text{-dpe})]^+ + e^-
\end{array}$$

scheme applies, but the $fac^+ \rightarrow mer^+$ isomerization step is so fast that it cannot be stopped completely on the voltammetric timescale even at −78 °C. Fig. 2c is a cyclic voltammogram at room temperature of a solution initially containing *fac*-$Cr(CO)_3(\eta^1$-dpe$)(\eta^2$-dpe$)$ which had been subjected to one scan of a cyclic voltammogram some 30 min earlier. This voltammogram displays only redox couple II, which shows that the bulk solution now contains only *mer*-$Cr(CO)_3$-$(\eta^2$-dpe$)(\eta^2$-dpe$)$. Although the conversion of *fac*-$Cr(CO)_3(\eta^1$-dpe$)(\eta^2$-dpe$)$ to *mer*-$Cr(CO)_3(\eta^1$-dpe$)(\eta^2$-dpe$)$ is not thermodynamically favoured, it occurs because *mer*-$[Cr(CO)_3(\eta^1$-dpe$)(\eta^2$-dpe$)]^+$ is involved in the cross redox reaction

$$\begin{array}{l}
mer\text{-}[Cr(CO)_3(\eta^1\text{-dpe})(\eta^2\text{-dpe})]^+ + fac\text{-}Cr(CO)_3(\eta^1\text{-dpe})(\eta^2\text{-dpe}) \rightleftharpoons \\
mer\text{-}Cr(CO)_3(\eta^1\text{-dpe})(\eta^2\text{-dpe}) + fac\text{-}[Cr(CO)_3(\eta^1\text{-dpe})(\eta^2\text{-dpe})]^+
\end{array}$$

However, the *fac*-$[Cr(CO)_3(\eta^1$-dpe$)(\eta^2$-dpe$)]^+$ generated by the cross redox reaction immediately isomerizes to *mer*-$Cr(CO)_3(\eta^1$-dpe$)(\eta^2$-dpe$)]^+$ so the reaction is repeated until all the *fac*-$Cr(CO)_3(\eta^1$-dpe$)(\eta^2$-dpe$)$ is converted to the mer^0 isomer. The same result is obtained if a minute quantity of chemical oxidant, such as $NOPF_6$, is added to a solution of the fac^0 isomer.

Analogous catalytic isomerizations have been observed for *fac*-$Cr(CO)_3$-$(P(OMe)_3)_3$ to *mer*-$Cr(CO)_3(P(OMe)_3)_3$ [27] and *cis,fac*-$Re(CO)_2(P_2P')Cl$ to *cis,mer*-$Re(CO)_2(P_2P')Cl$ [28].

Simply to emphasize the common occurrence of square schemes involving isomerization in the 17e configuration, we list here some of the starting materials which upon electrochemical or chemical oxidation give rise to behaviour similar to that described above: $M(CO)_3(PR_3)_2X$ (M = Mn, Re) [29]; $M(CO)_3(PR_3)_3$ (M = Cr, Mo, W) [30,31]; $Cr(CO)_3(P(OR)_3)_3$ [27]; $Cr(CO)_3(\eta^1$-dpm$)(\eta^2$-dpm$)$ [26]. The compounds $M(CO)_3$(L–E)X (M = Mn, Re; L–E = dpmS, dpmSe) undergo similar oxidations and isomerizations, but the resulting 17e cations containing sulphur and selenium are thermodynamically more stable [32]. In addition, there are other systems in which the initial isomerization of the 17e species occurs, but this is then followed by fast cross redox reactions, or coordination of a pendent donor atom or some other reaction, which competes with completion of the square scheme. Examples of these mechanisms will be discussed in subsequent sections. Reaction with the solvent or electrolyte also is possible, but the majority of our work has minimized these possibilities by using relatively non-coordinating solvents such as dichloromethane or acetone and electrolytes such as Bu_4NClO_4, Bu_4NPF_6 and Bu_4NBF_4 which contain anions which rarely act as ligands.

3. Disproportionation

There are many situations in which isomerizism to another thermodynamically preferred geometry is not possible and in non-coordinating solvents it has been found that disproportionation of the 17e species is the most common alternative reaction. Examples of 17e species which rapidly disproportionate at room temperature in non-coordinating solvents include $M(CO)_5X$ ($M = Cr$, Mo, W; $X =$ Cl, Br, I) [33,34], $Cr(CO)_5F$ [35], $V(CO)_6$ [36], $[Cr(CO)_2(\eta^6\text{-dam})]^+$ [37] and $[Cr(CO)_4(dpm)]^+$ [38].

Our first co-authored paper [33] was concerned with the electrochemical oxidation of $[Cr(CO)_5X]^-$ ($X = Cl$, Br, I) species. At room temperature in acetone solution $[Cr(CO)_5I]^-$ shows two one-electron oxidations, the first reversible and the second irreversible on the voltammetric timescale at a macroelectrode. At −78 °C both processes become fully reversible and this provided the first evidence for a Cr(II) halocarbonyl compound. The two redox processes are identified as

$$[Cr(CO)_5I]^- \rightleftharpoons Cr(CO)_5I + e^-$$

$$Cr(CO)_5I \rightleftharpoons [Cr(CO)_5I]^+ + e^-$$

In contrast, $[Mo(CO)_5I]^-$ gives a single irreversible two-electron oxidation response. This difference between chromium and molybdenum (and tungsten), and more generally between first row and second/third row transition metals, gradually emerged as a consistent theme. In this particular case the electrochemical oxidation products of $[Mo(CO)_5I]^-$ were not identified, but the electrochemical results could be explained in terms of a rapid disproportionation of the 17e species $Mo(CO)_5I$. Shortly afterwards, a study [34] of chemically generated $Cr(CO)_5I$ in acetone showed that it too disproportionates on the longer timescale upon warming, regenerating exactly half the molar amount of $[Cr(CO)_5I]^-$ with the remaining chromium being precipitated as a non-carbonyl containing product. Thus, the disproportionation

$$\begin{tikzcd} 2Cr(CO)_5I \arrow[r] & {[Cr(CO)_5I]^- + [Cr(CO)_5I]^+} \arrow[d] \\ & \text{decomposition products} \end{tikzcd}$$

reaction can be written as involving formation of an unstable 16e Cr(II) octahedral species as well as regenerating the starting material.

A major difference between carbonyl chemistry of the first and second/third row metals is the existence of an extensive chemistry of 18e seven coordinate species in the d^4 configuration for the heavy metals, but not for the first row elements. Thus Mo(II) and W(II), and to a lesser extent Re(III), have well-defined 7 coordinate carbonyl chemistry and this provides an additional thermodynamic driving force for the disproportionation of the 17e d^5 species of these metals. The 16e species resulting from the disproportionation can add a ligand to produce a relatively stable 18e seven coordinate species. A nice example of this is provided by the oxidations of $[Cr(CO)_5I]^-$ and $[Mo(CO)_5I]^-$ by iodine, the products being $Cr(CO)_5I$ and $[Mo(CO)_4I_3]^-$, respectively. In the chromium system the reaction is a simple redox process

$$[Cr(CO)_5I]^- \ 1/2I_2 \rightleftharpoons Cr(CO)_5I + I^-$$

The reactions involved in the molybdenum case are

$$[Mo(CO)_5I]^- I_2 \rightarrow Mo(CO)_5I + 2I^-$$

$$2Mo(CO)_5I \rightarrow [Mo(CO)_5I]^- [Mo(CO)_5I]^+$$

$$[Mo(CO)_5I]^+ + 2I^- \rightarrow [Mo(CO)_4I_3]^- + CO$$

In the presence of sufficient iodine the $[Mo(CO)_5I]^-$ is recycled until $[Mo(CO)_4I_3]^-$ is the only species present and the overall reaction is oxidative addition. However, mechanistic nuances of these reactions are unknown.

4. Oxidative additions

The existence of stable seven coordinate d^4 species for the second/third row metals provides for interesting comparisons with the first row metal chemistry. When the initial 18e octahedral complex contains a pendant (non-coordinated) donor atom this entity provides a readily available site to add to the metal following electrochemical oxidation, thus forming the higher coordinate d^4 product.

A series of compounds $M(CO)_3(\eta^1\text{-P–P})(\eta^2\text{-P–P})$ (M = Cr, Mo, W; P–P = dpm, dpe) were prepared and characterized by various spectroscopic techniques [26]. Upon electrochemical oxidation in both dichloromethane and acetone, *mer*-$Cr(CO)_3(\eta^1\text{-dpm})(\eta^2\text{-dpm})$ gives *mer*-$[Cr(CO)_3(\eta^1\text{-dpm})(\eta^2\text{-dpm})]^+$ (which slowly decomposes to *trans*-$[Cr(CO)_2(dpm)_2]^+$ [39]) whilst *fac*-$Cr(CO)_3(\eta^1\text{-dpe})(\eta^2\text{-dpe})$ gives unstable *fac*-$[Cr(CO)_3(\eta^1\text{-dpe})(\eta^2\text{-dpe})]^+$ which rapidly isomerizes to stable *mer*-$[Cr(CO)_3(\eta^1\text{-dpe})(\eta^2\text{-dpe})]^+$, and this is the expected behaviour.

Mer-$Mo(CO)_3(\eta^1\text{-dpm})(\eta^2\text{-dpm})$ exhibits quite different electrochemical properties as shown in Fig. 3. On the first oxidation scan in acetone there is an irreversible response at −0.180 V and on the reverse scan an irreversible reduction is observed at −0.740 V. Second and subsequent scans are identical. Controlled potential oxidative electrolysis at 0.380 V shows two electrons per molecule are consumed and the reductive cyclic voltammogram of the oxidized solution gives the irreversible response at −0.740 V and on the reverse scan the oxidative response at −0.180 V appears. Reductive controlled potential electrolysis of the previously oxidized solution also

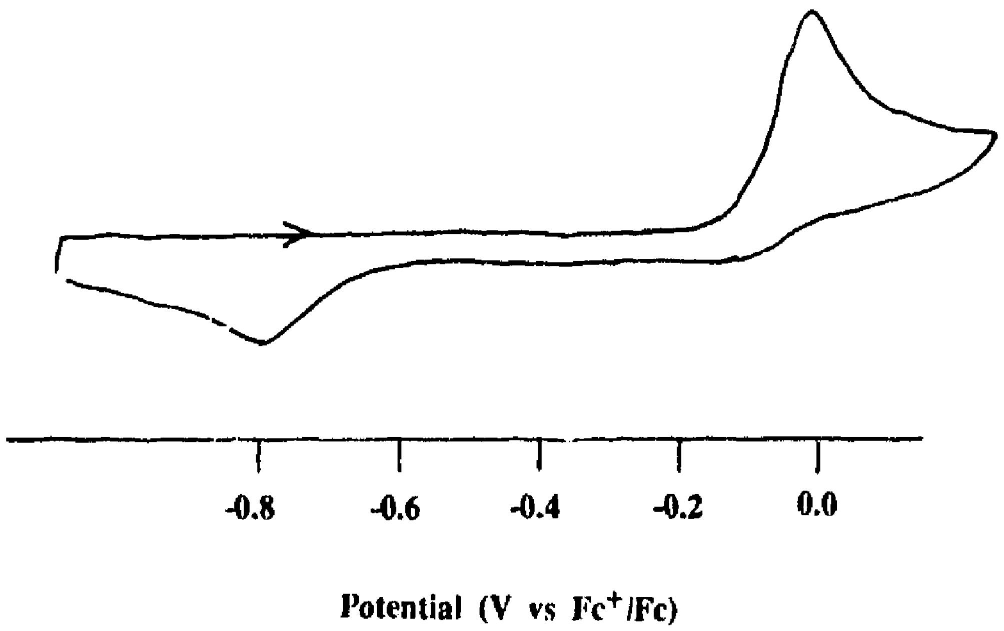


Fig. 3. Oxidative cyclic voltammogram at a Pt disk macroelectrode for the oxidation of *fac*-Mo(CO)$_3$(η^1-dpm)(η^2-dpm) in acetone (0.1M Et$_4$NClO$_4$) at 20 °C with a scan rate of 200 mV s^{-1} (adapted from Ref. [26]).

consumes two electrons per molecule and the voltammogram is identical to that of the starting material *mer*-Mo(CO)$_3$(η^1-dpm)(η^2-dpm). Thus the final products of the oxidation of *mer*-Mo(CO)$_3$(η^1-dpm)(η^2-dpm) and *mer*-Mo(CO)$_3$(η^1-dpm)(η^2-dpm) itself are interconvertible by electrolysis, but the overall processes are two-electron steps and the deceptively simple voltammograms obscure a complicated mechanism. Although the redox process is chemically reversible, it is not electrochemically reversible in the Nernstian sense because of the large potential difference between the processes. The behaviour of *fac*-Mo(CO)$_3$(η^1-dpe)(η^2-dpe) is slightly more complicated since it involves also the normal isomerization of *fac*-[Mo(CO)$_3$(η^1-dpe)(η^2-dpe)]$^+$ to *mer*-[Mo(CO)$_3$(η^1-dpe)(η^2-dpe)]$^+$, but it provides additional information since although the general behaviour is similar to that of the dpm complex, the two-electron process observed with the dpm complexes is now two separate one-electron steps, that is, the 17e intermediate can be observed. The overall mechanism proposed to explain these observations is

fac or *mer*-Mo(CO)$_3$(η^1-P-P)(η^2-P-P)$\rightarrow$
mer-[Mo(CO)$_3$(η^1-P-P)(η^2-P-P)]$^+$ $+e^-$

2*mer*-[Mo(CO)$_3$(η^1-P-P)(η^2-P-P)]$^+$ (17e)$\rightarrow$
mer-Mo(CO)$_3$(η^1-P-P)(η^2-P-P)(18e)+
mer-[Mo(CO)$_3$(η^1-P-P)(η^2-P-P)]$^{2+}$ (16e)

mer-[Mo(CO)$_3$(η^1-P-P)(η^2-P-P)]$^{2+}$ (16e)$\rightarrow$[Mo(CO)$_3$(η^2-P-P)$_2$]$^{2+}$ (18e)

in which the pendant phosphorus in the 16e *mer*-[Mo(CO)$_3$(η^1-P-P)(η^2-P-P)]$^{2+}$ coordinates to the metal to give the 18e seven coordinate species [Mo(CO)$_3$(η^2-P-P)$_2$]$^{2+}$. In the case of the dpe complex, the rate of disproportionation of the 17e intermediate was slow enough to allow its detection in the voltammograms. In a subsequent paper [40] the $[\mathrm{Mo(CO)_3(\eta^2\text{-}P\text{–}P)_2}]^{2+}$ species were isolated and fully characterized, thus confirming the validity of the overall mechanism, but surprisingly the 18e species $[\mathrm{Mo(CO)_3(\eta^2\text{-}P\text{–}P)_2}]^{2+}$ slowly decomposed to the formally 16e complex $[\mathrm{Mo(CO)_2(\eta^2\text{-}P\text{–}P)_2}]^{2+}$. However, this type of reaction is not without precedent as $\mathrm{Mo(CO)_3(PPh_3)_2Cl_2}$ loses CO to give $\mathrm{Mo(CO)_2(PPh_3)_2Cl_2}$ [41], as does $\mathrm{Mo(CO)_3(S_2CNEt_2)_2}$ to give $\mathrm{Mo(CO)_2(S_2CNEt_2)_2}$ [42].

Additional nuances of the electrochemical mechanism were revealed by a still later study [43] using microelectrode techniques. Oxidation of *mer*-$\mathrm{W(CO)_3(\eta^1\text{-}dpm)(\eta^2\text{-}dpm)}$ at a 25 μm radius platinum microdisk electrode was still a single two-electron process, but at a 3 μm radius microelectrode two one-electron processes are observed. Detailed steady state and fast scan voltammetric studies showed there are competing pathways to the final product. The first step is

$$mer\text{-}\mathrm{W(CO)_3(\eta^1\text{-}dpm)(\eta^2\text{-}dpm)} \rightarrow mer\text{-}[\mathrm{W(CO)_3(\eta^1\text{-}dpm)(\eta^2\text{-}dpm)}]^+ + e^-$$

followed by

$$mer\text{-}[\mathrm{W(CO)_3(\eta^1\text{-}dpm)(\eta^2\text{-}dpm)}]^+ (17e) \rightarrow [\mathrm{W(CO)_3(\eta^2\text{-}dpm)_2}]^+ (19e)$$

and

$$[\mathrm{W(CO)_3(\eta^2\text{-}dpm)_2}]^+ (19e) \rightarrow [\mathrm{W(CO)_3(\eta^2\text{-}dpm)_2}]^{2+} (18e) + e^-$$

or

$$\begin{array}{l} mer\text{-}[\mathrm{W(CO)_3(\eta^1\text{-}dpm)(\eta^2\text{-}dpm)}]^+ (17e) \rightarrow [\mathrm{W(CO)_3(\eta^1\text{-}dpm)(\eta^2\text{-}dpm)}]^{2+} (16e) + e^- \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad [\mathrm{W(CO)_3(\eta^2\text{-}dpm)_2}]^{2+} (18e) \end{array}$$

with both the 17e and 19e transient intermediates being observed on the short microelectrode voltammetric timescale.

Analogous products are formed by the electrochemical or chemical oxidation of a series of complexes $\mathrm{W(CO)(NO)(\eta^1\text{-}L\text{–}L)(\eta^2\text{-}L\text{–}L)I}$ (L–L = dpm, dpe, ape, dpmS, dpmSe, apeS, apeSe) [44]. Although the details of the reactions vary with ligand and sometimes two one-electron processes are observed and in other cases a single two-electron process is observed, the final stable product is always 16e *trans*-$[\mathrm{W(NO)(\eta^2\text{-}L\text{–}L)_2I}]^{2+}$ with $[\mathrm{W(CO)(NO)(\eta^1\text{-}L\text{–}L)(\eta^2\text{-}L\text{–}L)I}]^+$ and $[\mathrm{W(CO)(NO)(L\text{–}L)_2I}]^{2+}$ (structure unknown) sometimes being observed as intermediates. Interestingly, in these systems disproportionation appears to be slow, especially for those complexes containing sulphur and selenium ligands.

5. Voltammetry at microelectrodes

5.1. *Fast reactions*

The concept of exchange averaged spectra is well known in NMR spectroscopy where deceptively simple spectra result when an exchange reaction of some kind occurs which is fast compared with the NMR timescale. The usual response to this difficulty is to cool the solution so that the exchange becomes slow on the NMR timescale and in favourable cases the slow exchange limiting spectrum can then be observed. Analogous phenomena occur in electrochemistry but they are not so widely recognised. We have already seen how isomerization reactions can be slowed at low temperatures, but for those reactions discussed so far the isomerization and cross redox reactions have been comparatively slow. However, there are a number of systems for which such reactions are much faster and cooling the solution does not slow the processes sufficiently to allow a complete electrochemical study at conventional (macro) electrodes, exactly analogous to the NMR situation when the slow exchange limit cannot be reached. Fortunately, electrochemists have available a range of techniques which have widely differing timescales, and in particular the use of microelectrodes (radius < 25 μm) [23] allows study of electrode processes on a much shorter timescale.

The systems based upon the compounds *fac*-M(CO)$_3$(η^3-P$_2$P′) (M = Cr, Mo, W) are well suited to study with microelectrodes because isomerization and cross redox reactions are fast [45,46]. Fig. 4a shows a cyclic voltammogram (scan rate 100 mV s^{-1}) for a solution of *fac*-Cr(CO)$_3$(P$_2$P′) in dichloromethane (0.1M Bu$_4$NClO$_4$) at a platinum macrodisk electrode (radius 0.9 mm) at 20 °C. Redox couple I appears to be a simple reversible one-electron process and an obvious interpretation would be that redox couple I is due to the reaction

$$fac\text{-Cr(CO)}_3\text{(P}_2\text{P}') \rightleftharpoons fac\text{-[Cr(CO)}_3\text{(P}_2\text{P}')]^+ + e^-$$

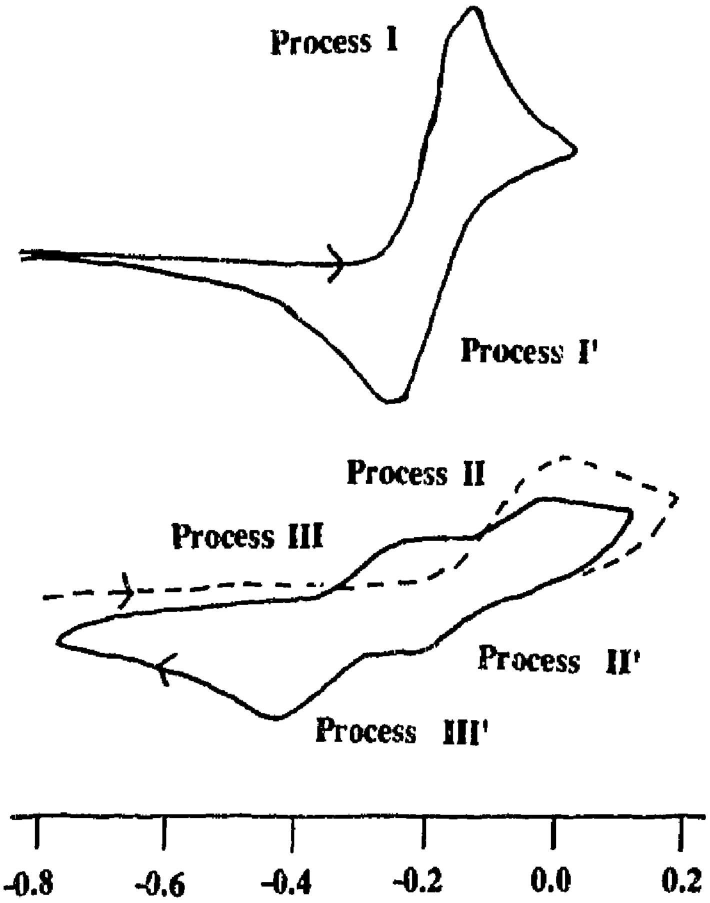


Fig. 4. Oxidative cyclic voltammogram at a Pt disk macroelectrode for the oxidation of *fac*-Cr(CO)$_3$(P$_2$P′) in dichloromethane (0.1M Bu$_4$NClO$_4$) with a scan rate of 100 mV s^{-1}. (a) At 20 °C, (b) at −45 °C (- - - is first scan) (adapted from Ref. [27]).

implying that *fac*$^+$ is completely stable on the voltammetric timescale at room temperature, which would be unusual. However, when the temperature is lowered to −45 °C (Fig. 4b) two separate reversible redox responses (II and III) are observed instead of one. This type of behaviour was unexpected since electrochemical processes are usually simplified at low temperatures. In fact the cyclic voltammogram at −45 °C is due to the normal square scheme

$$\begin{array}{ccc}
\mathit{fac}\text{-Cr(CO)}_3(\mathrm{P_2P'}) & \rightleftharpoons & \mathit{fac}\text{-}[\mathrm{Cr(CO)_3(P_2P')}]^+ + e^- \\
\upharpoonleft\downharpoonright & & \upharpoonleft\downharpoonright \\
\mathit{mer}\text{-Cr(CO)}_3(\mathrm{P_2P'}) & \rightleftharpoons & \mathit{mer}\text{-}[\mathrm{Cr(CO)_3(P_2P')}]^+ + e^-
\end{array}$$

but in this system the isomerization between *fac* and *mer* is extremely rapid in both the 17e and 18e configurations. In addition the cross redox reaction

$$\mathit{fac}\text{-Cr(CO)}_3(\mathrm{P_2P'}) + \mathit{mer}\text{-}[\mathrm{Cr(CO)_3(P_2P')}]^+ \rightleftharpoons \mathit{fac}\text{-}[\mathrm{Cr(CO)_3(P_2P')}]^+ + \mathit{mer}\text{-Cr(CO)}_3(\mathrm{P_2P'})$$

also is fast. These factors combine to give such rapid equilibria between the various species that at room temperature a macroelectrode detects only an average response.

Detailed studies at various scan rates with microelectrodes reproduce and extend these observations. Using a Pt microdisk electrode (radius 25 μm) at a scan rate of 5 V s^{-1} gives a single reversible response (couple I), at 200 V s^{-1} redox couples II and III are observed (corresponding to Fig. 4b at a macroelectrode) and at a scan rate of 2000 V s^{-1} only redox couple II is observed which is genuinely due to the *fac*$\rightleftharpoons$*fac*$^+$ couple. At this scan rate the electrochemical timescale outruns the isomerization reaction. Generally similar observations were made for the corresponding molybdenum and tungsten complexes. This system behaves in this unusual way because there are steric pressures in both the *fac* and *mer* geometries of $\mathrm{M(CO)_3(P_2P')}$ which distort the usual balance between electronic and steric preferences. In the *fac* geometry there is considerable steric interaction between phenyl rings on the two terminal phosphorus atoms of $\mathrm{P_2P'}$, whilst in the *mer* isomer there is considerable strain in the angles about the central phosphorus atom. Thus, the complexes are subject to strain in both configurations and are not completely stable in either isomeric form in both the 17e and 18e configurations. As well as making the isomerization reactions fast, these factors also have the interesting result of making the 17e *mer*$^+$ and *fac*$^+$ isomers of comparable stability – the first time this has been observed. All of the rate constants and equilibrium constants for this system were determined by a combination of direct measurement and simulation techniques which involved writing special programs [45]. It has since been demonstrated that "Digisim" [4] easily simulates the behaviour of this system giving parameters which agree with our earlier values [47].

In a subsequent paper [46] the $\mathrm{Cr(CO)_3(P_2P')}$ system was used to demonstrate the advantages of using both steady state and fast scan techniques at microelectrodes and a new design for an electrochemical cell coupled to new electronic circuitry was described which allows a more accurate subtraction of the background current and correction for uncompensated resistances.

The $[Cr(CO)_4\{P(OMe)_3\}_2]^{0/+}$ system provides an example for which even microelectrode voltammetry fails to provide a sufficiently short timescale to distinguish between the electrochemical responses of the *cis* and *mer* isomers. Spectroscopic evidence (^{31}P NMR and IR) shows the presence of both 18e isomers and the addition of small amount of $[Cr(CO)_4\{P(OMe)_3\}_2]^+$ causes the signal for both isomers to broaden, not just one. This and other evidence leads to the conclusion that the interconversion of cis^+ and $trans^+$ is so fast that it outruns even the microelectrode timescale [48].

5.2. *Thermodynamic studies*

The 18e compound $Cr(CO)_2(dpe)_2$ can exist as both *cis* and *trans* isomers and in solution their relative proportions depend upon the solvent. The 17e cation *trans*-$[Cr(CO)_2(dpe)_2]^+$, readily formed by air oxidation, considerably complicates spectroscopic measurements on the solutions. There is an unfortunate double coincidence of IR frequencies as the single carbonyl stretches of *trans*-$Cr(CO)_2(dpe)_2$ and *trans*-$[Cr(CO)_2(dpe)_2]^+$ occur at very similar frequencies to the two stretches of *cis*-$Cr(CO)_2(dpe)_2$, so IR spectroscopy is not useful for this system. The paramagnetic *trans*-$[Cr(CO)_2(dpe)_2]^+$ undergoes rapid self-exchange with *trans*-$Cr(CO)_2(dpe)_2$ and it also drives the fast cross redox reaction

$$trans\text{-}[Cr(CO)_2(dpe)_2]^+ + cis\text{-}Cr(CO)_2(dpe)_2 \rightleftharpoons trans\text{-}Cr(CO)_2(dpe)_2 + cis\text{-}[Cr(CO)_2(dpe)_2]^+$$

which complicate ^{31}P NMR measurements of the equilibrium between cis^0 and $trans^0$.

Steady state voltammetry at microelectrodes was the only technique which allowed simultaneous determination of the concentration of $trans^0$, cis^0 and $trans^+$ species in a wide range of solvents, thus allowing various thermodynamic and kinetic parameters to be evaluated [10].

6. Photoelectrochemistry

We have several times noted in early papers that 17e carbonyl species seem to be light sensitive; examples include *mer*-$[Mn(CO)_3(PR_3)_2X]^+$ [29], *trans*-$[Cr(CO)_4(PR_3)_2]^+$ [27], $[Cr(CO)_4(dpm)]^+$ [38], *mer*-$[Cr(CO)_3(P(OR)_3)_3]^+$ [31]. In many cases, but not all, the presence of light promotes disproportionation of the 17e species to generate half a mole equivalent of the corresponding 18e compound and the remainder of the metal content is converted to non-carbonyl material presumably via an unstable 16e intermediate. The singly oxidized cation of *mer,mer*-$\{Cr(CO)_3(\eta^2\text{-}dpe)\}_2(\mu\text{-}dpe)$ [49] is also light sensitive but the resultant reaction is cleavage of the dpe bridge and formation of a variety of products from the two fragments.

Only recently have we begun systematic studies of photoelectrochemistry in collaboration with R.G. Compton and his group at Oxford University, but the early indications are that there is an extensive photochemistry of both 18e and 17e carbonyl compounds. The photoelectrochemistry is investigated in a flow system using channel electrodes and kinetic parameters are determined by varying both scan rate and flow rate.

The first compound to be investigated [50] was the familiar *fac*-$Mn(CO)_3(dpm)Cl$ and in the absence of light the electrochemistry in the flow system was exactly the same as described earlier under stationary conditions. When the electrode was irradiated with light, oxidation of *mer*-$Mn(CO)_3(dpm)Cl$ was observed even on the first scan and it was shown that *fac*-$Mn(CO)_3(dpm)Cl$ is photoisomerized to the mer^0 isomer. In addition, the current due to the oxidation of *fac*-$Mn(CO)_3(dpm)Cl$ was enhanced relative to that in the dark and after considering a number of theoretical models it was deduced that the only one which was in quantitative accord with the data was one involving an ECE type of photodisproportionation process.

$$fac\text{-}Mn(CO)_3(dpm)Cl \rightleftharpoons fac\text{-}[Mn(CO)_3(dpm)Cl]^+ + e^-$$

$$2fac\text{-}[Mn(CO)_3(dpm)Cl]^+ \rightarrow fac\text{-}Mn(CO)_3(dpm)Cl + fac\text{-}[Mn(CO)_3(dpm)Cl]^{2+}$$

$$\downarrow h\nu$$

$$mer\text{-}Mn(CO)_3(dpm)Cl$$

The Mn(III) cation *fac*-$[Mn(CO)_3(dpm)Cl]^{2+}$ is known to be unstable as it is the product of the irreversible oxidation response at high positive potential previously noted in the cyclic voltammetry of *fac*-$Mn(CO)_3(dpm)Cl$, and therefore the disproportionation step can be considered to be irreversible. Thus, two new processes, namely photoisomerization of *fac*-$Mn(CO)_3(dpm)Cl$ and photodisproportionation of *fac*-$[Mn(CO)_3(dpm)Cl]^+$ were discovered in this well-studied system.

Electrochemical oxidation of $Cr(CO)_6$ in acetonitrile solution in the dark gives two oxidation responses, one reversible and one irreversible. Under irradiation with light, three new processes are observed and these were shown to be due to the one-electron oxidations of $Cr(CO)_5(CH_3CN)$, $Cr(CO)_4(CH_3CN)_2$ and $Cr(CO)_3(CH_3CN)_3$ which are formed by photochemical substitution of $Cr(CO)_6$ [51]. In the same paper it was shown that *trans*-$[Cr(CO)_2(dpe)_2]^{2+}$, formed by electrochemical oxidation of *trans*-$[Cr(CO)_2(dpe)_2]^+$, undergoes photodisproportionation.
This is the first time we have observed disproportionation of a 16e compound.

$$2trans\text{-}[Cr(C)_2(dpe)_2]^{2+} \rightarrow trans\text{-}[Cr(CO)_2(dpe)_2]^+ + trans\text{-}[Cr(CO)_2(dpe)_2]^{3+}$$

$$\downarrow$$

decomposition products

The photovoltammetric technique using channel electrodes was applied to *fac*-$Mo(CO)_3(P_2P')$ but in this case only photoisomerization to the *mer*^{0} isomer was observed, and there was no photodisproportionation or photofragmentation [52].

7. Solid state voltammetry

Metal carbonyl derivatives are generally insoluble in, and chemically inert to water. We have shown recently that *cis*-$Cr(CO)_2(dpe)_2$, *trans*-$Cr(CO)_2(dpe)_2$ and *trans*-$[Cr(CO)_2(dpe)_2]^+$ may be mechanically attached to a carbon electrode and upon immersion of the electrode in water containing an electrolyte, good electrochemical responses from the carbonyl species are observed [53,54]. The redox processes involved are similar to those observed in organic solutions, but in the solid state the isomerization of *cis*$^+$ to *trans*$^+$ is much slower and *cis*$^+$ has been identified directly on the electrode surface by FTIR techniques [54]. The experimental results are in accord with an electrochemical process that takes place at the solid–solution interface to form a layer of oxidized material. Electron transfer is postulated to occur by electron hopping via self exchange and cross redox reactions with the rate being dependent on the state of the electrode-compound–solution interface and the surface charge. Nucleation and crystal growth phenomena also are believed to accompany the electron transfer and ion-migration processes.

8. General summary

In probably all cases the first step in the metal based electrochemical oxidation of carbonyl systems is a single electron process. Those responses which appear to be single two-electron processes, usually for second/third row metals, result from rapid disproportionation following an initial one-electron transfer. It follows therefore that the behaviour of each system is dominated by the chemistry of its paramagnetic 17e derivatives. The lifetimes of these species vary widely, with those of the first row elements (Cr, Mn) in general being longer lived than those of the corresponding derivatives of the second/third row transition metals. There seems to be a tendency for the 17e species to be more stable as the number of carbonyl ligands decrease, thus $Cr(CO)_5I$ is stable only at low temperature but numerous tricarbonyl 17e chromium cations can be isolated at room temperature. Similarly, while species such as *trans*-$[Mo(CO)_2(dpe)_2]^+$ can be isolated, 17e molybdenum species with more carbonyl ligands are much less stable [30]. The stability of the 17e complexes determines which techniques may be used to characterize them and very unstable species may be detectable only by short timescale techniques. Voltammetric methods alone based upon oxidation of the precursor generally do not give direct structural information for short lived species, but electrochemical oxidation combined with *in situ* ESR spectroscopy or electrochemical oxidation via "tip oxidation" ESMS [55] may provide additional information. Longer lived 17e species may be readily characterized by additional electrochemical techniques as well as by all the usual spectroscopic techniques, especially ESR and IR. Although ^{31}P NMR spectroscopy is not normally applicable to the study of paramagnetic species, we have found the fast electron self exchange reaction between isomeric 18e and 17e species to be useful for identifying the isomeric form of the 17e species. Thus, for example, the presence of *trans*-$[Cr(CO)_2(dpe)_2]^+$ in solution broadens the signal due to *trans*-$Cr(CO)_2(dpe)_2$ but not that of *cis*-$Cr(CO)_2(dpe)_2$ [10]. Similar effects can occasionally be observed in ESR spectra; thus the sharp ESR spectrum of *mer*-$[Cr(CO)_3\{P(OMe)_3\}_3]^+$ is unaffected by addition of *fac*-$Cr(CO)_3\{P(OMe)_3\}_3$ but addition of *mer*-$Cr(CO)_3\{P(OMe)_3\}_3$ causes the spectrum to collapse [31].

The potential at which the first oxidation of an 18e metal carbonyl derivative occurs is also subject to certain trends. For any series of metal complexes in which carbonyl groups are substituted by phosphine or phosphite ligands the potential of the first oxidation generally becomes less positive as the number of carbonyl groups decreases, but there are wide variations depending upon the nature of the ligand and the isomeric form of each compound. Similarly, compounds containing halide ligands are usually oxidized at less positive potentials than isoelectronic species without halides, e.g. $[Cr(CO)_5I]^-$ is more easily oxidized than $Cr(CO)_6$ [33,35].

It is also generally true that first row metal derivatives are more easily oxidized than their second/third row analogues. Thus $[Cr(CO)_5I]^-$ is more easily oxidized than $[M(CO)_5I]^-$ (M = Mo, W) [33], $Cr(CO)_2(dpm)_2$ is more easily oxidized than $M(CO)_2(dpm)_2$ [43] and the carbonyl halide derivatives of manganese are more easily oxidized than their rhenium analogues [29].

Finally, some thoughts on areas of interest in the near future. The techniques of photoelectrochemistry and solid state chemistry of samples attached to electrodes are just being developed for metal carbonyl compounds and are expected to yield further interesting insights concerning the redox and chemical properties of these systems. Simultaneous electrochemistry and ESR measurements is now a standard technique, but for metal carbonyls simultaneous electrochemistry and FTIR spectroscopy can be further developed [56]. We have already successfully coupled electrochemical measurements with ESMS [57] (although not yet using metal carbonyl derivatives) and the extreme sensitivity of ESMS will be particularly useful. Chemical systems of interest in the future are likely to include dimeric species, carbonyl fluoride and carbonyl hydride compounds. The dimers enable aspects of communication of metal centres to be explored, while hydrides and fluorides may provide access to stable higher oxidation states since these ligands cannot themselves be oxidized under normal conditions.

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