

The effect of 19-electron formation constants on the electrochemistry and electron transfer induced substitution reactions of cyclopentadienylmetal halide complexes

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Abstract

The reduction of cyclopentadienylmetal halide complexes is generally considered to involve addition of an electron to an orbital that is antibonding with respect to the metal–halide bond. Subsequent metal–halide bond cleavage yields the halide and an organometallic radical. At inert electrodes, this radical is reduced further to an 18-electron anion. This series of reactions constitutes a prototypical ECE mechanism. Chemical reduction can be used to divert the radical into other pathways such as electron transfer chain catalyzed substitution. Attempts to initiate such reductively induced substitution reactions of $\text{CpFe}(\text{CO})_2\text{I}$ and $\text{Cp}'\text{Mo}(\text{CO})_3\text{I}$ give very different results, suggesting that these very similar complexes are reduced via substantially different mechanisms. Very likely, the molybdenum complex reacts via a DISP mechanism instead of ECE. The difference in electrochemical reduction mechanism as well as the different reactivity toward reductively induced substitution are explained in terms of a difference in the formation constants of 19-electron intermediates. © 2006 Elsevier B.V. All rights reserved.

Keywords: Iron; Molybdenum; Cyclopentadienyl; Iodide; Reduction; Formation constant

1. Introduction

The electrochemical reduction of organometallic halide complexes containing a combination of π - and σ -bonding ligands, such as $\text{CpM}(\text{CO})_n\text{X}$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$; $\text{M} = \text{Fe}, \text{Mo}, \text{W}$), has long been proposed to involve addition of the extra electron to an orbital which is antibonding with respect to the metal–halide bond [1–6]. Consequently, reduction has been assumed to be followed by rapid metal–halide bond cleavage to produce a 17-electron organometallic radical and a halide ion. At mercury electrodes, the organometallic fragment reacts with the electrode to yield a mercury-bridged dimer, $[\text{CpM}(\text{CO})_n]_2\text{Hg}$, which can be further reduced to the 18-electron anion, $[\text{CpM}(\text{CO})_n]^-$. At inert electrodes such as platinum or carbon, which do not react with the 17- e^- species, a two-

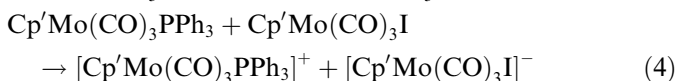
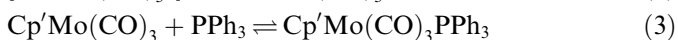
electron reduction directly producing the 18- e^- organometallic anion and halide is observed. The second electron transfer occurs because reduction of the 17- e^- fragment is typically easier than that of the halide complex. Another possible reaction of the 17- e^- intermediate would be dimerization, but it has been demonstrated both experimentally and theoretically that when a reducible odd-electron species is formed at an electrode following an initial electron transfer, the second electron transfer is so fast that even a diffusion controlled dimerization cannot compete with it [7].

The 18-electron anions produced by the direct electrochemical reduction of the halide complexes at inert electrodes are stable, and thus relatively unreactive. Much research in recent years has demonstrated that odd-electron, 17- e^- and 19- e^- , organometallic species are highly reactive and are involved as critical intermediates in many important reactions [8]. By using a chemical reductant or a mediator instead of an electrode to perform reductions, it is possible to generate and take advantage of the reactivity of

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the odd-electron intermediates formed by a one-electron transfer, which at an electrode would not have significant lifetimes because of the rapidity of the second electron transfer. We have used such a procedure for initiating the electron transfer chain catalyzed (ETC) substitution of phosphine for halide on $\text{CpFe}(\text{CO})_2\text{X}$ complexes [9].

As part of our ongoing study of the electron transfer induced reactivity of transition metal organometallic compounds, we have been attempting to extend the ETC substitution of phosphine for halide to molybdenum complexes. Logically, one would expect $\text{Cp}'\text{Mo}(\text{CO})_3\text{I}$ ($\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{CH}_3$) to participate in the same type of reductively induced substitution with PPh_3 as the analogous iron complex, $\text{CpFe}(\text{CO})_2\text{I}$, does:



Initiation by a chemical reductant in Eq. (1) should produce quantitative substitution via a cycle consisting of Eqs. (2)–(4). However, while $\text{CpFe}(\text{CO})_2\text{I}$ undergoes this reaction rapidly and quantitatively, $\text{Cp}'\text{Mo}(\text{CO})_3\text{I}$ does not. Details of the reductively induced substitution reactions of $\text{Cp}'\text{Mo}(\text{CO})_3\text{I}$ will be presented elsewhere. Here, we would like to address the question of why $\text{Cp}'\text{Mo}(\text{CO})_3\text{I}$ does not react in the same way as $\text{CpFe}(\text{CO})_2\text{I}$. We propose that the difference originates with the different equilibrium constants for Eq. (2) and that this difference also leads to a difference in the mechanism of the two compounds' electrochemical reductions.

2. Experimental

2.1. Reagents

$\text{Mo}(\text{CO})_6$ obtained from Strem Chemicals and methylcyclopentadiene dimer obtained from Acros Organics were used to synthesize $[\text{Cp}'\text{Mo}(\text{CO})_3]_2$ by the published procedure [10]. $\text{Cp}'\text{Mo}(\text{CO})_3\text{I}$ was then synthesized from $[\text{Cp}'\text{Mo}(\text{CO})_3]_2$ by the published procedure [11]. $\text{CpFe}(\text{CO})_2\text{I}$ was purchased from Aldrich Chemicals. CH_3CN was distilled from CaH_2 under nitrogen. The supporting electrolyte for electrochemical experiments, $[\text{Bu}_4\text{N}]\text{PF}_6$, was obtained from Alfa Aesar and was dried at 100°C under vacuum before use. All other reagents were obtained commercially and were used as received.

2.2. Instrumentation

IR spectra were collected using a Mattson Instruments Genesis II FTIR and a cell with CaF_2 windows separated by a 0.1 mm spacer. Cyclic voltammetry was performed using a Bioanalytical Systems BAS 100B/W electrochemical analyzer and controlled potential electrolysis using a

CH Instruments 1140 Electrochemical Analyzer. Solutions contained approximately 0.1 M $[\text{Bu}_4\text{N}]\text{PF}_6$ supporting electrolyte. Cyclic voltammetry was done using a 0.5 mm Pt disc working electrode, Pt wire auxiliary electrode, and Ag wire quasi-reference electrode. Controlled potential electrolyses were performed in a nitrogen-atmosphere glove box using 25×25 mm platinum foil working and auxiliary electrodes and a silver wire quasi-reference electrode in an H-cell with compartments separated by a medium porosity glass frit. All potentials are expressed relative to the formal potential of the ferrocenium–ferrocene couple (Fc^+/Fc).

3. Results and discussion

3.1. Cyclic voltammetry of $\text{CpFe}(\text{CO})_2\text{I}$ and $\text{Cp}'\text{Mo}(\text{CO})_3\text{I}$

Fig. 1 shows the cyclic voltammograms of FpI ($\text{Fp} = \text{CpFe}(\text{CO})_2$) and MpI ($\text{Mp} = \text{Cp}'\text{Mo}(\text{CO})_3$) in CH_3CN . FpI is irreversibly reduced at a platinum disc electrode at a peak potential of -1.50 V vs. Fc^+/Fc at 0.2 V s^{-1} (Fig. 1a). The chemical irreversibility of the reductions of Fp -halide complexes has been established to be the result of rapid dissociation of the halide following electron transfer [1–3]. The formation of I^- from FpI is evidenced by two oxidation peaks on the reverse CV scan at ca. 0.0 and $+0.1$ V (not shown), corresponding to the two-step oxidation of iodide to triiodide and then iodine typically observed in nonaqueous solvents [12]. The other initial product of the reduction of FpI is expected to be Fp , which may react chemically with the electrode (in the case of Hg [1–3]), be further reduced to Fp^- , or dimerize to Fp_2 . At platinum electrodes only the latter two options are available. The dissociation of iodide after reduction is presumed

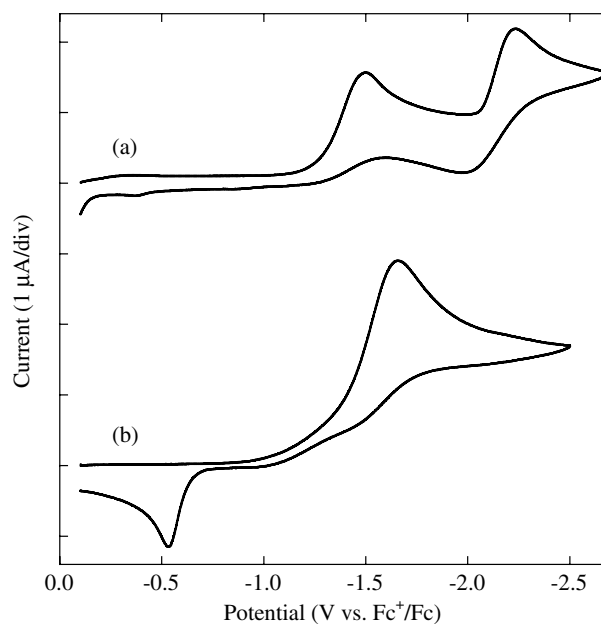


Fig. 1. Cyclic voltammograms of 1×10^{-3} M (a) FpI and (b) MpI in $\text{CH}_3\text{CN}/[\text{Bu}_4\text{N}]\text{PF}_6$ (0.1 M) at a Pt disc electrode at 0.2 V s^{-1} .

to occur so quickly that the Fp is formed in the immediate vicinity of the electrode surface, and at the potentials necessary for reduction of FpI the Fp is reduced to the Fp⁻ anion ($E_{\text{Fp}}^{\circ} = -1.27 \text{ V}$ [13]). However, the Fp⁻ anion is known to react rapidly with FpI to yield the dimer Fp₂ [2,14,15]. The Fp may also dimerize directly to Fp₂. The forward rate constant for dimerization of Fp is essentially diffusion-controlled ($\geq 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in cyclohexane and benzene [16,17]). However, Amatore et al., have demonstrated both theoretically and experimentally that even for species which dimerize this rapidly, dimerization cannot compete effectively with reduction for reducible species formed near an electrode at a potential negative of the species' reduction potential [7]. Thus the dimerization of Fp is not believed to contribute significantly to the mechanism of the electrochemical reduction of FpI.

Therefore, even though the initially formed Fp undergoes a second electron transfer, the only organometallic product expected from the electrochemical reduction of FpI is the one-electron product Fp₂. This is confirmed by the observation of a second irreversible reduction in the CV of FpI at a peak potential of -2.23 V , matching that of known Fp₂ under the same conditions. The mechanism of the reduction of FpI thus appears to involve fundamentally an ECE process (Electrochemical reduction of FpI, Chemical dissociation of iodide, Electrochemical reduction of Fp) coupled with the rapid reaction of the initial product, Fp⁻, with starting material to yield the Fp₂ dimer as the final product. Thus, while the electrochemical reduction of FpI is a two-electron process, the coupling of this reduction with the chemical cross-reaction of the reduction product with starting material yields a net one-electron reduction. All of the chemical reactions coupled to the electron transfers for FpI are so rapid that no significant changes were observed in the cyclic voltammograms at scan rates of up to 300 V s^{-1} [18].

The cyclic voltammogram of MpI in CH₃CN (Fig. 1b) is fundamentally different from that of FpI. MpI displays a single chemically irreversible reduction with a peak potential of -1.66 V and a peak current about twice that of FpI under the same conditions. On the reverse scan the voltammogram of MpI displays an anodic peak at -0.53 V which corresponds to the oxidation of Mp⁻, as verified by comparison with an authentic sample prepared by reduction of Mp₂. This difference in voltammetric response does not necessarily indicate a difference in reduction mechanism. The reaction between anion and the iodide complex is much slower for molybdenum than for iron. One literature source indicates no reaction occurs between CpMo(CO)₃Cl and [CpMo(CO)₃]⁻ [14], while another reports that the reaction of CpMo(CO)₃Br with [CpMo(CO)₃]⁻ is more than 10^5 times slower than that for the corresponding iron complexes [15]. It would be anticipated that Cp'Mo(CO)₃I and the anion would react similarly slowly. Thus on the basis of cyclic voltammetric results alone, it is still possible that the fundamental mechanism for MpI reduction is ECE, but unlike the FpI system it is not coupled

to a rapid anion + iodide complex reaction. As with FpI, no significant changes in the cyclic voltammograms of MpI were observed at scan rates of up to 300 V s^{-1} .

3.2. Controlled potential electrolysis experiments

The cyclic voltammograms of the two dimers, Fp₂ and Mp₂, in CH₃CN showed chemically irreversible reductions (-2.26 V for Fp₂; -1.75 V for Mp₂) coupled to anodic peaks on the reverse scans for oxidation of the corresponding anions (-1.30 V for Fp⁻; -0.52 V for Mp⁻), in good agreement with the literature [13]. Controlled potential electrolyses in CH₃CN at potentials approximately 200 mV more negative than the CV peak potentials consumed two electrons per mole of dimer reduced (2.0 F/mol for Fp₂; 1.9 F/mol for Mp₂) to produce the anions, identified by cyclic voltammetry and IR spectra. Controlled potential electrolyses at potentials 200 mV more positive than the oxidation potentials for the resulting anions regenerated the dimers with the consumption of approximately one electron per mole of anion (0.85 F/mol for Fp⁻; 0.97 F/mol for Mp⁻). These results are completely consistent with previous reports of the electrochemistry of these and related organometallic dimers [13].

A significant difference was observed when the electrolyses were performed in the presence of iodide. Controlled potential oxidation of anion solutions formed by reduction of the dimers followed by addition of ten equivalents of [Bu₄N]I consumed 0.81 F/mol for Fp⁻ but 1.9 F/mol for Mp⁻. Furthermore, while the product of Fp⁻ oxidation in the presence of iodide was still Fp₂, Eq. (5), the product from Mp⁻ oxidation changed to MpI, Eq. (6), as identified by its IR spectrum:



The Mp⁻ anion was also generated by reduction of MpI, producing Mp⁻ and one equivalent of iodide. Controlled potential oxidation of Mp⁻ in this solution consumed 1.7 F/mol and produced both MpI and a small amount of Mp₂. These key observations, by the principle of microscopic reversibility, illuminate an important difference between the mechanisms of reduction of FpI and MpI.

3.3. Comments on the reduction mechanisms

The individual steps proposed to be involved in the reduction of either FpI or MpI, further abbreviated as MI, are shown in the following equations:



The sequence of reactions in Eqs. (7)–(9) corresponds to the ECE mechanism assumed to apply to all such complexes at inert electrodes. Eq. (11) shows the “reproportionation” reaction which is very rapid for iron but very slow for molybdenum [2]. In chemically initiated or mediated ETC substitution reactions, the lower effective concentration of reducing agent (e^-) decreases the probability of Eq. (9) occurring and allows the intermediate 17- e^- radical (M) to participate in the substitution reaction. It should be noted that for FpI, ETC substitution is not observed when the reducing agent is an electrode because of the high effective concentration of electrons and the fact that the M radical is formed very close to the electrode surface, where it is immediately reduced to the unreactive anion before it can participate in the substitution reaction. The other key to the success of the ETC substitution reaction for FpI is the very large value of the equilibrium constant for Eq. (8). It has been estimated that the formation constant for the 19- e^- [FpI] $^-$ complex is approximately $10^{-4} M^{-1}$ [18], and so when this species is formed by reduction of FpI it will rapidly and essentially quantitatively dissociate to Fp and iodide.

The reason that we chose to study Cp'Mo(CO)₃I instead of CpMo(CO)₃I is that the formation constants for the 19- e^- [Cp'Mo(CO)₃X] $^-$ complexes have been determined [19], and that for [MpI] $^-$ was reported to be approximately $200 M^{-1}$. Assuming this value is accurate, the equilibrium in Eq. (8) would be expected to lie to the left for molybdenum, giving the 19- e^- [MpI] $^-$ anion significant stability. Under those circumstances, even using mediated reduction or a chemical reductant, the concentration of 17- e^- Mp would be much lower than that of the corresponding iron complex and it therefore would not be as available to participate in ETC substitution reactions. In fact, under conditions where FpI undergoes rapid and quantitative ETC substitution to yield [FpPPh₃] $^+$, MpI reacts slowly or not at all and yields completely different products (Cp'Mo(CO)₂(PPh₃)I and [Cp'Mo(CO)₃I] $^-$). The substitution reaction of MpI which produces Cp'Mo(CO)₂(PPh₃)I is believed to involve atom transfer chain catalysis [20]. These results will be the subject of a future communication.

Now consider the oxidation of the anionic complexes. As expected, oxidation of both Mp $^-$ and Fp $^-$ consumes 1 F/mol and produces the dimer of each. However, when Mp $^-$ is oxidized in the presence of iodide, both the product and the electron stoichiometry change. Instead of being a simple one-electron oxidation to dimer, the reaction becomes a two-electron oxidation to form MpI. This observation may be easily explained by the reverse of Eqs. (9), (8) and (7). Oxidation of the Mp $^-$ produces the 17- e^- Mp, which in the presence of iodide forms the 19- e^- [MpI] $^-$ complex, presumably in a rapid equilibrium [8]. This complex is then readily oxidized by a second electron to form MpI. As with the reduction reactions, since this reaction is expected to be thermodynamically favorable, and since the rapid equilibrium forms [MpI] $^-$ near the elec-

trode surface, the oxidation reaction occurs before even a diffusion-controlled dimerization can take place.

Returning again to the reduction of MpI, it therefore seems likely that the mechanism is not dominated by the ECE pathway, Eqs. (7)–(9), but instead by the DISP mechanism, Eqs. (7) and (10), with which all ECE reactions are in competition [21]. The disproportionation reaction, Eq. (10), may involve either reaction between two 19- e^- anions or, because of electrostatic repulsion, reduction of a neutral 17- e^- radical by a 19- e^- anion. The rapid equilibration between the 17- and 19-electron species makes either route possible [8]. In fact, ECE and DISP mechanisms are always in competition and which one predominates can be difficult or impossible to determine conclusively [21a]. But on the basis of all the evidence presented above, it seems likely that the primary pathway for the molybdenum complex is DISP, while that for iron is ECE.

4. Conclusions

The reduction of cyclopentadienylmetal halide complexes typically produces the corresponding anionic metal complex and halide through, at least initially, a two-electron process. While it might be reasonably anticipated that the iron and molybdenum systems would react similarly, there are key differences. The relative nucleophilicities of the [CpM(CO)_n] $^-$ anions cause their ultimate fates to differ. But more importantly for reactions which seek to take advantage of the odd-electron intermediates formed during the reduction of these complexes, the formation constants for the 19- e^- species are different and lead to very different reactivity under circumstances (chemical reduction or mediated electron transfer) which allow an opportunity for participation in reactions other than electron transfer. Since the 19- e^- iron complex, [CpFe(CO)₂I] $^-$, is thermodynamically unstable, it efficiently produces the 17- e^- fragment which can participate in substitution reactions. On the other hand, the 19- e^- molybdenum complex, [Cp'Mo(CO)₃I] $^-$, is relatively stable, sequestering the molybdenum in a form that cannot participate in the desired substitution reaction. This difference in reactivity illustrates the importance of understanding the formation constants of odd-electron organometallic complexes.

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