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Electrochemistry of Tricarbonyl(η^6-1,3,5-cycloheptatriene)metal(0) Complexes of the Group 6B Elements in Aprotic Media

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Abstract

The electrochemistry of tricarbonyl(η^6-1,3,5-cycloheptatriene)chromium(0), -molybdenum(0) and -tungsten(0) was studied at a Pt electrode in aprotic solvents. It was observed that the electrochemical behaviour of these complexes is different in acetonitrile and dichloromethane possibly due to different coordination abilities of the solvent molecules. For the determination of the number of electron transfers at their respective peak potentials, a coulometric method was used. It was found that only one electron transfer occurs at the first oxidation peak of each complex.

Introduction

Tricarbonyl(η^6-1,3,5-cycloheptatriene)chromium(0) (**1**), -molybdenum(0) (**2**) and -tungsten(0) (**3**) were isolated from the thermal reaction of tricarbonyltris(acetonitrile)metal(0) and cycloheptatriene and studied stereochemically two decades ago [1–5]. They have been used as starting materials in the synthesis of various organometallic compounds [6].

Although many substitution and addition reactions have been carried out on the cycloheptatriene ligand in these complexes [6], their electrochemical behaviour has not been studied extensively, except for a few reports on the measurement of half-wave potentials of **1** and **2** [7, 8]. The aim of this study is to investigate the electrochemical behaviour of complexes **1**–**3**.

The electrochemical behaviour of **1**–**3** was studied by using the cyclic voltammetric (CV) technique in acetonitrile and dichlorometane solutions containing 0.1 M tetrabutylammonium tetrafluroborate (TBAFB) as the supporting electrolyte. Oxidation–reduction potentials of these complexes were measured *versus* Ag/Ag$^+$ reference electrode. Constant potential electrolysis at the measured oxidation potentials was carried out to determine the number of electron transferred.

Experimental

Reagent grade dichloromethane and acetonitrile were dried over calcium hydride and distilled under nitrogen. TBAFB (Aldrich) was used as received from the manufacturer.

Complexes **1**–**3** were synthesized according to a previously reported method [3] under a dry nitrogen atmosphere. They were purified using column chromatography on silica gel and recrystallized from n-hexane. IR and NMR spectroscopic methods were used for their identification.

A Tacussel pilot-type servoit and a Tacussel potentiostat (type PRT 30-0.1) were used to programme the potential and the recordings were made with a Sefran TRP XY/yt recorder. A Pt bead working electrode, Pt wire counter electrode and a Ag/Ag$^+$ (0.01 M) reference electrode were used for cyclic voltammetry studies. These three electrodes were positioned as close to each other as possible, in order to minimize IR drop. Details of the cyclic voltammetry system have been given elsewhere [9].

Cyclic voltammograms were taken under a nitrogen atmosphere in acetonitrile or dichloromethane in quiet solutions at room temperature.

Controlled-potential electrolyses at the anodic peak potentials of the complexes were performed using the same apparatus. A divided cell was used for this purpose, with a Ag/Ag$^+$ electrode used as the reference electrode and Pt foils employed as the working and secondary electrodes.

Equal amounts of 0.1 M TBAFB were placed in both cell compartment, the electrolysis cell was purged with nitrogen followed by distilled dichloromethane or acetonitrile, and the complex was introduced into the cell.

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The cell was connected to the potentiostat and the recorder and potentiostat were switched on simultaneously, in order to follow the current decay with time.

IR spectra of the complexes before and after constant-potential electrolyses were detected with a Perkin-Elmer 1430 IR spectrophotometer.

Results and Discussion

The electrochemistry of complexes **1**–**3** was studied at a Pt electrode in the aprotic solvents acetonitrile and dichloromethane containing 0.1 M TBAFB as the supporting electrolyte. The oxidation and reduction peak potentials of complexes **1**–**3**, measured in acetonitrile and dichloromethane solutions are given in Tables 1 and 2 respectively. The voltammetric data in Table 1 indicate that **2** and **3** have a similar electrochemical behaviour while **1** is somewhat different in acetonitrile. However, all of the complexes behave similarly in dichloromethane (Table 2).

Electrochemical Oxidation of Complexes 1–3

A cyclic voltammogram of the oxidation of **2** in acetonitrile at 25 °C is shown in Fig. 1. At the first anodic scan, (Fig. 1a) an oxidation peak (I_a) occurs at +0.5 V *versus* Ag/Ag$^+$. If the scan is then reversed, a reduction peak (I_c) appears. Together, these two peaks constitute an electrochemically reversible one electron redox couple. In the cyclic voltammograms, the oxidation and reduction branches give peaks of

TABLE 1. Cyclic Voltammetric Data for Complexes 1–3 and Hexacarbonylmetal(0) Complexes[a] in Acetonitrile

Compound	No.	$E_{p,a}$ (V *vs.* Ag/Ag$^+$)	$E_{p,c}$ (V *vs.* Ag/Ag$^+$)
$Cr(CO)_3(C_7H_8)$	1	+0.8	reversible
		+1.75	−0.1
		+2.30	−2.3
$Cr(CO)_6$		+1.65	reversible
		+2.30	
$Mo(CO)_3(C_7H_8)$	2	+0.5	reversible
		+0.8	−0.15
		+1.25	−0.50
		+1.7	−2.40
		+2.30	
$Mo(CO)_6$		+1.70	
		+2.40	
$W(CO)_3(C_7H_8)$	3	+0.35	reversible
		+0.80	−0.1
		+1.20	−2.35
		+1.75	
		+2.25	
$W(CO)_6$		+1.75	
		+2.15	

[a] At a Pt electrode in acetonitrile solutions with 10^{-3} M substrate concentration and 0.1 M TBAFB at 25 °C. Scan rate: 200 mV/s. Peak potential in volts *vs.* Ag/Ag$^+$.

TABLE 2. Cyclic Voltammetric Data for Complexes 1–3[b] in Dichloromethane

Compound	No	$E_{p,a}$ (V *vs.* Ag/Ag$^+$)	$E_{p,c}$ (V *vs.* Ag/Ag$^+$)
$Cr(CO)_3(C_7H_8)$	1	+1.25	−2.35
$Mo(CO)_3(C_7H_8)$	2	+1.10	
$W(CO)_3(C_7H_8)$	3	+1.25	−2.30

[b] At a Pt electrode in dichloromethane solutions with 10^{-3} M substrate concentration and 0.1 M TBAFB at 25 °C. Scan rate: 200 mV/s. Peak potentials in volt *vs.* Ag/Ag$^+$.

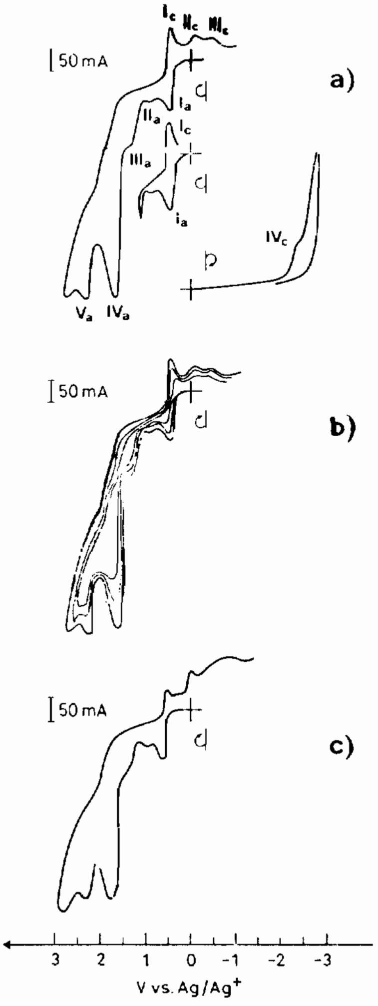

Fig. 1. Cyclic voltammograms of complex **2** in CH_3CN (0.1 M TBAFB) at 25 °C: (a) first scan, scan rate 200 mV/s; (b) after several scans, scan rate 200 mV/s; (c) scan rate 250 mV/s.

equal heights (Fig. 1a). If the anodic scan is continued, four irreversible peaks ($\mathrm{II_a}$–$\mathrm{V_a}$) are observed at more positive potentials.

It is observed that the shape and position of the oxidation peaks were critically dependent on the treatment of the Pt electrode surface and scan rates. Only with careful cleaning of the electrodes and saturation of the solutions with dry N_2, could a response similar to that shown in Fig. 1a be observed. In addition, after a few scans the peaks are broadened, shifted to more positive potentials, and reduced in intensity (Fig. 1b) with respect to the initial scan (Fig. 1a). We suggest that the electrode surface is coated by decomposition products causing ill-defined peaks. The shape and position of the peaks are affected by changing the scan rate. An increase in the scan rate, caused all peaks to broaden and shift towards more anodic potentials (Fig. 1c).

Figure 2 shows a cyclic voltammogram of **3** in acetonitrile (CH_3CN) at 25 °C. As was found with **2** an electrochmically reversible one electron redox couple is obtained at the first positive potential. If the anodic scan was continued, irreversible peaks were observed at more positive potentials. The cyclic voltammograms indicate that complexes **2** and **3** have a similar electrochemical behaviour in acetonitrile.

Figure 3 shows a cyclic voltammogram of **1** in acetonitrile at 25 °C. At the first scan to positive potentials, three oxidation peaks were observed, two less than had been found during the first anodic scan of either **2** or **3**. This may be due to the fact that the initial intermediates of **2** and **3** are highly reactive with respect to the nucleophilic attack of acetonitrile, which can be attributed to the greater tendency of molybdenum and tungsten than chromium to allow seven coordination with acetonitrile and hence any cation formed from **2** or **3** will be more prone to nucleophilic attack, than those formed from **1**. The complex formation of the electrochemically-generated cation with acetonitrile is shown in reaction (1).

$$[\mathrm{M(CO)_3(C_7H_8)}]^+ + \mathrm{CH_3CN} \longrightarrow [\mathrm{M(CO)_3(C_7H_8)(CH_3CN)}]^+ \qquad (1)$$

M = Mo, W.

The cyclic voltammograms of complexes **1**–**3** in dichloromethane at 25 °C are shown in Fig. 4. It is seen that all three complexes behave similarly in dichloromethane, while they have a different behaviour in acetonitrile. This may be attributed to the different coordination ability of dichloromethane and acetonitrile molecules.

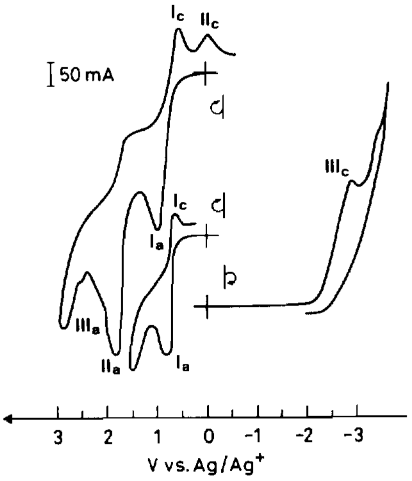

Fig. 3. Cyclic voltammograms of complex **1** in CH_3CN (0.1 M TBAFB) at 25 °C. Scan rate: 200 mV/s.

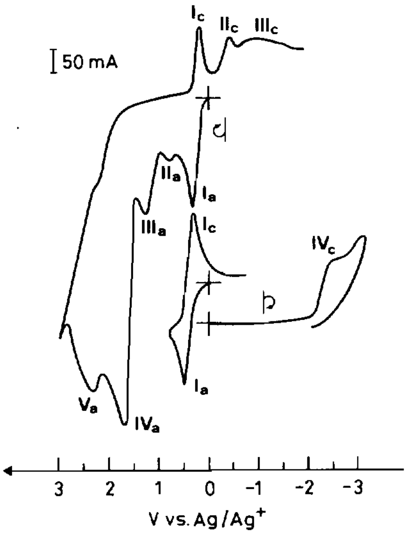

Fig. 2. Cyclic voltammograms of complex **3** in CH_3CN (0.1 M TBAFB) at 25 °C. Scan rate: 200 mV/s.

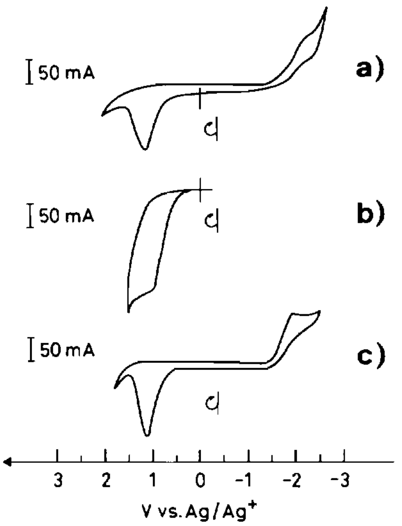

Fig. 4. Cyclic voltammograms of complexes **1** (a), **2** (b) and **3** (c) in CH_2Cl_2 at 25 °C. Scan rate: 200 mV/s.

Electrochemical Reduction of 1–3

A cyclic voltammogram for the reduction of **2** is given in Fig. 1a. When the first cathodic scan is recorded, only one reduction peak is observed at -2.4 V (IV_c) *versus* Ag/Ag^+. However, if the anodic scan is completed, three additional reduction peaks are obtained at -0.15 (II_c), -0.5 (III_c), and -2.4 (IV_c) *versus* V Ag/Ag^+. The reduction peaks of II_c and III_c are found to be related to the oxidation peaks, since the cyclic voltammogram of pure 1,3,5-cycloheptatriene has very broad reduction peaks in this cathodic region (II_c and III_c). Peaks at II_c and III_c are assumed to arise from the reduction of free cycloheptatriene ligand released by rearrangement of the coordination sphere of the metal upon oxidation. Identical behaviour is observed for complexes **1** and **3** under the same conditions (Figs. 2 and 3).

In order to determine the number of electrons involved at the reduction or oxidation peaks in the cyclic voltammograms, the controlled-potential electrolysis at Pt electrodes in acetonitrile and dichloromethane was performed. During the electrolysis a scan of the current as a function of time is obtained. The number of coulombs passed during the electrolysis is calculated from the area under the curve. It is found that only one electron transfer occurs at the first oxidation peaks of complexes **1–3** (Table 3). The oxidation mechanism of the complexes at first oxidation peaks are given by reaction (2).

$$M(CO)_3(C_7H_8) \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [M(CO)_3(C_7H_8)]^+ \qquad (2)$$

M = Cr, Mo, W.

Although the constant-potential electrolyses were done at the other oxidation peak potentials of **1–3**, the number of electron transfers could not be determined, because the working electrode was coated by decomposition products at higher peak potentials.

The last two oxidation peak potentials of complexes **1–3** have values similar to those of the corresponding hexacarbonyl complexes (Table 1). Therefore, it is assumed that complexes **1–3** in acetonitrile may be converted into hexacarbonyl complexes before these peak potentials. This is proved by the IR spectroscopic study. IR spectra of **2** in acetonitrile show three absorption bands in the region of carbonyl stretching indicating a *fac*-$M(CO)_3$ unit (Fig. 5a) [10].

TABLE 3. The Number of Electron Transfers in Complexes 1–3 at First Oxidation Peak Potential in Acetonitrile

Compound	No.	$E_{p,a}$ (V *vs.* Ag/Ag^+)	n_1
$Cr(CO)_3(C_7H_8)$	1	+0.8	1
$Mo(CO)_3(C_7H_8)$	2	+0.5	1
$W(CO)_3(C_7H_8)$	3	+0.35	1

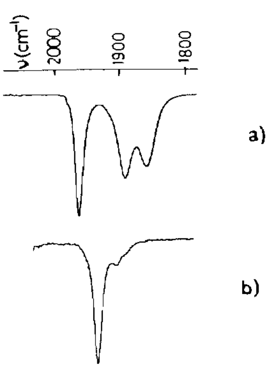

Fig. 5. IR spectrum of complex 2 in CH_3CN solution, showing carbonyl stretching: (a) before electrolysis, (b) after electrolysis at +1.75 and +2.3 V *vs.* Ag/Ag^+.

Figure 5b shows the IR spectrum of **2** which is taken after the electrolysis of the complex at +1.75 or +2.3 V *versus* Ag/Ag^+ and gives only one absorption band at 1985vs cm^{-1} for hexacarbonyl molybdenum(0). This indicates that complex **2** is converted into hexacarbonylmolybdenum(0) before these oxidation potentials.

This study shows that complexes **1–3** have a different electrochemical behaviour depending upon the solvent. Complexes **1–3** are converted into hexacarbonylmetal(0) through the complex ion $[M(CO)_3(C_7H_8)]^+$ in acetonitrile as an intermediate after electolysis at the appropriate potential. Their electrochemical study in dichloromethane also results in the formation of $[M(CO)_3(C_7H_8)]^+$. However, its conversion into hexocarbonylmetal(0) is not observed.

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