Electrochemical Study of Tricarbonyl(\(\eta^6\)-cyclooctatetraene)metal(0) Complexes of the Group 6 Elements

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Dedicated to Professor Cornelius G. Kreiter on the occasion of his 60th birthday

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Carbonyl, Chromium, Molybdenum, Tungsten, Cyclic Voltammetry

Tricarbonyl(\(\eta^6\)-cyclooctatetraene)metal(0) complexes of the group 6 elements were prepared by using the procedures described in the literature with some minor modifications and identified by IR and NMR spectroscopy. Their electrochemical behavior was studied by using cyclic voltammetry in dichloromethane solution containing 0.1 M tetrabutylammonium tetrafluoroborate as supporting electrolyte. Their oxidation and reduction potentials were measured and discussed in terms of the frontier energy levels in connection with the UV-Visible electronic absorption spectral data. In order to elucidate the mechanism of electrooxygenation of the complexes, constant potential electrolysis was performed for one representative example, tricarbonyl(\(\eta^6\)-cyclooctatetraene)chromium(0). The IR monitoring of the reaction showed that it is gradually converted to hexacarbonylchromium(0) upon electrolysis at constant potential.

Introduction

Transition metal complexes containing cyclic polyolefins have been used to promote some interesting catalytic reactions like hydrogenation and cycloaddition [1]. The latest developments in research testing catalytic reactions like hydrogenation and cycloaddition have been used to promote someintermediate transformations with alkynes or dienes [9]. Complexes of the group 6 elements of cyclic polyolefins the largest number contain the cyclooctatetraene ligand, denoted as COT. Owing to the presence of four olefinic bonds in the presence of transition metals. Of the metal derivatives of cyclic polyolefins the largest number contain the cyclooctatetraene ligand, denoted as COT. Owing to the presence of four olefinic bonds and the possibility of becoming planar as [COT]2- or adopting several other configurations, COT can form a large number of transition metal complexes [2]. Complexes with chromium, molybdenum, and tungsten carbonyls are of two principal types, M(CO)3(\(\eta^6\)-COT) and M(CO)3(\(\eta^5\)-COT) (M = Cr, Mo, W). The first attempt to prepare M(CO)3(\(\eta^5\)-COT) complexes, in analogy to Fe(CO)3(\(\eta^5\)-COT) [3], yielded the M(CO)3(\(\eta^6\)-COT) complexes (M: Cr, Mo, W) as sole products [4]. The crystal and molecular structure of Mo(CO)3(\(\eta^6\)-COT), established by X-ray crystallography [5], is consistent with the suggested hexahapto coordination of the cyclooctatetraene ring. Soon after the isolation of hexahapto coordinated cyclooctatetraene complexes, Mo(CO)3(\(\eta^6\)-COT) has been shown to react reversibly with carbon monoxide to give the corresponding Mo(CO)3(\(\eta^5\)-COT) complex which has the cyclooctatetraene ligand coordinated to the transition metal through two alternating C=C bonds in a tub conformation [6]. Later, it has been shown that the photochemical reaction of hexacarbonyltungsten(0) and cyclooctatetraene at -20°C gives the analogous W(CO)3(\(\eta^5\)-COT) complex in high yields [7]. Temperature dependent NMR spectroscopic studies have shown that the M(CO)3(\(\eta^6\)-COT) complexes have fluxional behavior, undergoing a hindered rotation of the cyclooctatetraene ligand with respect to the remaining fac-M(CO)3 moiety of the molecule [8]. Chromium and molybdenum complexes of cyclooctatetraene have been shown to undergo cycloaddition reactions with alkynes or dienes [9]. Complexes of the type Mo2(CO)4(\(\mu^2\)-\(\eta^5\)-\(\eta^5\)-COT)2 have also been well characterized [10]. Despite of the early synthesis and structural characterization of the M(CO)3(\(\eta^6\)-COT) complexes of group 6 elements, their electrochemical behavior has not been examined yet. This may be attributed to the general instability of the cyclic polyolefin complexes. Here, we report the results of an electrochemical study on

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the tricarbonyl($\eta^6$-cyclooctatetraene)metal(0) complexes of group 6 elements.

The electrochemistry of many group 6 metal carbonyls has been studied under different aspects. A few examples to be mentioned are ligand influence on the electronic properties of olefin substituted metal carbonyls [11], electrochemical reduction of metal carbonyls [12], redox reactions of metal carbonyls [13], and electron transfer catalysis [14]. Group 6 metal carbonyl derivatives have been shown to undergo simple oxidation, a one electron transfer reaction, upon electrolysis at constant potential [15].

\[ [\text{M(CO)}_{6-n}\text{L}_n] = [\text{M(CO)}_{6-n}\text{L}_n]^+ + e^- \quad (1) \]

M: Cr, Mo, W; L: Ligands other than CO; n: 0, 1, 2

The electrochemical behavior of the known tricarbonyl($\eta^6$-cyclooctatetraene)-metal(0) complexes of the group 6 elements were studied by cyclic voltammetry in dichloromethane solution containing 0.1 M tetrabutylammonium tetrafluoroborate as a supporting electrolyte. In order to elucidate the mechanism of electrooxidation, constant potential electrolysis of Cr(CO)$_3$(COT) was performed at the first anodic potential. The electrochemical reaction was followed by taking the FTIR spectrum of the solution in the course of electrolysis. Also, the effect of the central atom (Cr, Mo, W) on the redox behavior of the complexes was studied.

**Experimental**

All reactions and manipulations involving the metal carbonyl complexes were carried out either in vacuum or under dry inert atmosphere (N$_2$ or Ar). Solvents were distilled after refluxing over metallic sodium or phosphorus pentoxide under nitrogen for several days. Cyclooctatetraene, mesitylene, hexacarbonylchromium(0) hexacarbonylmolybdenum(0), and hexacarbonyltungsten(0) (Aldrich) were available commercially and used without further purification. Photochemical reactions were carried out in an immersion-well apparatus [16] (solidex glass, $\lambda > 280$ nm) by using a Hanau TQ 150 high pressure mercury lamp, which was cooled by circulating water or precooled methanol. Tricarbonyl($\eta^6$-cyclooctatetraene)metal(0) complexes of the group 6 elements were prepared by using the procedures given in the literature [4, 7] with some modifications. Tricarbonyl(tris(acetonitrile)chromium(0) [17] as in the original procedure [4], and tricarbonylmesitylenemolybdenum(0) [18] instead of the original tricarbonyldiglymmemolybdenum(0) were used as the labile starting complexes for the preparation of tricarbonyl($\eta^6$-cyclooctatetraene)chromium(0) and tricarbonyl($\eta^6$-cyclooctatetraene)molybdenum(0), respectively. Tricarbonyl($\eta^6$-cyclooctatetraene)tungsten(0) was synthesized by extended UV irradiation of hexacarbonyltungsten(0) and cyclooctatetraene in $n$-hexane at -20°C [7]. Isolation and purification of the complexes were done by recrystallization from $n$-hexane and/or column chromatography. The complexes were identified by IR and NMR spectroscopy.

NMR spectra were recorded on a Bruker DPX 400 spectrometer (400.132 MHz for $^1$H, 100.613 MHz for $^{13}$C) using TMS as internal reference for both $^1$H and $^{13}$C. Perkin-Elmer 16 PC FTIR and 1430 IR spectrophotometers were used to record the infrared spectra of the complexes from their $n$-hexane or dichloromethane solutions. Cyclic voltammograms of the complexes were taken by using a Potentiocan Wenking POS 73 type potentiostat and recorded on a Lloyd PL3 xy recorder.

The electrochemical behavior of the complexes was studied by using cyclic voltammetry in dichloromethane solution containing 0.1 M tetrabutylammonium tetrafluoroborate, (n-Bu)$_4$NBF$_4$, (TBAFB) as supporting electrolyte. The redox potentials of these complexes were measured at a Pt-bead (working) electrode versus a Ag wire reference electrode. A Pt wire was used as counter electrode. The oxidation potential of the Fe(II)/Fe(III) couple against Ag-wire was found to be 0.55 V. All of the studies were carried out at room temperature with a scan rate 200 mV/s, and always a background CV was carried out first. Dichloromethane was found to be inert towards the complexes studied under the conditions of the experiment. However, the use of acetonitrile caused formation of acetonitrile complexes due to ligand exchange reactions. In order to elucidate the mechanism of electrooxidation, constant potential electrolysis of Cr(CO)$_3$(COT) was performed at the first anodic potential in a H-type cell. Since Ag wire was used as reference, a negligible potential drift was adjusted during the course of constant potential electrolysis. The electrochemical reaction was followed by monitoring the FTIR spectrum before and after the electrolysis. ESR spectra were recorded on a Varian E 12 spectrometer at -20°C during the electrolysis of the Cr(CO)$_3$(COT) solution in dichloromethane.

Generally, nitrogen or argon gas was allowed to pass through the solution before each recording to avoid the interference of the reduction waves of oxygen with the waves obtained for the compounds. The surface of the solution was blanketed by nitrogen or argon gas during recording to prevent reentry of oxygen. CV studies were made under nitrogen or argon atmosphere in dichloromethane, in quiet medium, at room temperature.
Table 1. Oxidation and reduction peak potentials of the complexes in dichloromethane at a scan rate of 200mV/s.

<table>
<thead>
<tr>
<th>Complex Formula</th>
<th>$E_{pa}$ (V)</th>
<th>$E_{pc}$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(CO)$_3$(COT)</td>
<td>I$_a$ 0.75</td>
<td>I$_c$ -0.30</td>
</tr>
<tr>
<td></td>
<td>II$_a$ 1.35</td>
<td>I$_c$ -1.75</td>
</tr>
<tr>
<td></td>
<td>III$_a$ -0.50</td>
<td></td>
</tr>
<tr>
<td>Mo(CO)$_3$(COT)</td>
<td>I$_a$ 0.80</td>
<td>I$_c$ -1.65</td>
</tr>
<tr>
<td></td>
<td>II$_a$ 1.70</td>
<td></td>
</tr>
<tr>
<td></td>
<td>III$_a$ -0.50</td>
<td></td>
</tr>
<tr>
<td>W(CO)$_3$(COT)</td>
<td>I$_a$ 0.90</td>
<td>I$_c$ -1.60</td>
</tr>
<tr>
<td></td>
<td>II$_a$ 1.65</td>
<td></td>
</tr>
<tr>
<td></td>
<td>III$_a$ -0.50</td>
<td></td>
</tr>
<tr>
<td>Cr(CO)$_6$</td>
<td>I$_a$ 1.65</td>
<td></td>
</tr>
<tr>
<td>Mo(CO)$_6$</td>
<td>I$_a$ 1.71</td>
<td></td>
</tr>
<tr>
<td>W(CO)$_6$</td>
<td>I$_a$ 1.77</td>
<td></td>
</tr>
</tbody>
</table>

Results and Discussion

Although the electrochemical behavior of the group 6 hexacarbonylmetals(0) has already been studied in aprotic solvents [12, 15, 19], we have also measured the oxidation potentials of three metal carbonyls in our solvent-electrolyte system for the purpose of comparison with those of M(CO)$_3$(COT) complexes. The oxidation peak potentials of M(CO)$_6$ complexes measured in dichloromethane are given in Table 1 together with the redox peak potentials of M(CO)$_3$(COT) (M: Cr, Mo, W). Although in acetonitrile solution hexacarbonylchromium(0) has been found to be oxidized reversibly to [Cr(CO)$_6$]$^+$ which is an exceptionally stable 17-electron species [19a], its oxidation in dichloromethane is quasi-reversible. The mechanism given in the literature for the oxidation of Cr(CO)$_6$ [19a, 20] can be adopted for the oxidation of M(CO)$_6$ in dichloromethane as follows.

$$\begin{align*}
\text{M(CO)}_6 & \rightarrow \text{M(CO)}_6^{+} + e^- \\
2\text{M(CO)}_6^{2+} & \rightarrow \text{M(CO)}_6^{+} + \text{M(CO)}_6
\end{align*}$$

or

$$\begin{align*}
\text{M(CO)}_6^{2+} & \rightarrow \text{M(CO)}_6^{+} + e^- \\
\text{M(CO)}_6^{2+} & \rightarrow \text{M}^{2+} + 6\text{CO}
\end{align*}$$

A brief inspection of the data given in Table I reveals that the oxidation potentials (I$_a$ and II$_a$) as well as reduction potentials (I$_c$ and II$_c$) are characteristic of the metal carbonyl complexes.

![Cyclic voltammogram of Cr(CO)$_3$(COT) in dichloromethane at room temperature, a) anodic scan, b) peak clipping after $I_a$, and c) cathodic scan, at a scan rate of 200 mV/s.](image.png)

A close inspection of Table I shows that the first oxidation potential of the three hexacarbonylmetal(0) complexes increases on descending the group, which is attributed to an increase in the metal-ligand $\pi$ interaction on passing from chromium to tungsten [21].

The cyclic voltammogram of Cr(CO)$_3$(COT) in dichloromethane at 25°C is depicted in Fig. 1 as an example. The anodic scan is characterized by two anodic peaks (I$_a$ and II$_a$) at 0.75 and 1.35 V versus the Ag wire reference electrode (Fig. 1a). No coupled cathodic peak was observed upon reversal of the scan direction even at rates up to 1000 mV/s. Upon wave clipping after I$_a$ (Fig. 1b) a cathodic peak (I$_c$) appears at -0.30 V versus Ag wire. This reduction peak was observed only in the case of the chromium complex. The cathodic scan from 0.0 to -2.0 V versus Ag wire (Fig. 1c) was characterized by a reduction peak (I$_c$) at -1.75 V which is coupled with an anodic peak (II$_c$) at -0.5 V versus Ag wire. After several anodic scans the first oxidation peak (I$_a$) loses intensity whereas the second oxidation peak (II$_a$) gains intensity. This may be due to the consumption of the complex during the measurement.

A plot of peak current versus square root of voltage scan rate, $\nu^{1/2}$, is given in Fig. 2. A linear relationship was found between $\nu^{1/2}$ and the first anodic ($I_a$) and the first cathodic ($I_c$) currents in the range of scan rates used (100 to 1000 mV/s), indicating diffusion controlled electron exchange reactions at $I_a$ and $I_c$ for all three complexes.

A close inspection of Table I reveals that the oxidation potentials (I$_a$ and II$_a$) as well as reduction
Electrochemical Study of Tricarbonyl(η⁶-cyclooctatetraene)metal(0) Complexes

The potentials ($I_c$) have similar values for all the M(CO)$_3$(η⁶-COT). However, a slight positive shift was observed in both the first oxidation potential and the first reduction potentials on going from Cr through W. The latter observation can be explained in terms of the increasing extend of π-bonding on descending in the group [15a]. The increasing π interaction causes the metal atom to become more positively charged which facilitates the reduction and impedes the oxidation. Comparing $I_a$ values for the M(CO)$_3$(η⁶-COT) complexes with the first oxidation potential of the corresponding hexacarbonylmetal(0), one recognizes a decrease in the first oxidation potential upon substitution of CO by the weaker π-acceptor ligand, COT. After the substitution, σ-donation and π-back bonding between the metal and ligand become less effective and the HOMO energy level of the complexes increases.

The increase in the first oxidation potentials of the hexacarbonylmetal(0) complexes on descending in the group can be correlated to their electronic absorption spectra. Hexacarbonylmetal(0) complexes give two absorption bands in the region of 300-400 nm which are assigned to the spin forbidden d-d transitions, and the transition energy increases on going from chromium to tungsten [22]. For a d-d transition in the octahedral complexes, both HOMO and LUMO are predominantly of metal d-orbital character. The lowest energy UPS bands (Ultraviolet Photoelectron Spectroscopy) of the hexacarbonylmetal(0) complexes also show that their ionization energies increase in the same order [23]. This indicates that the HOMO energy level is lowered by going from chromium to tungsten. Therefore, the oxidation peak potential of hexacarbonylmetal(0) increases in the same order, as expected.

The wavelengths of the absorption bands observed in the UV-visible electronic spectra are given in Table II. The weak lowest energy bands given in the last column are most probably due to the forbidden d-d transitions. The wavelength of these absorption bands decreases on going from chromium to tungsten, i.e. the energy increases in the order Cr < Mo < W, as in the case of the hexacarbonylmetal(0) complexes.

In order to elucidate the mechanism of electrooxidation, constant potential electrolysis was carried out for one representative complex, tricarbonyl(η⁶-cyclooctatetraene)chromium(0), at the first oxidation potential of 0.75 V versus Ag wire in dichloromethane solution. The course of the electrolysis was followed by taking the IR spectra. A solution of Cr(CO)$_3$(η⁶-COT) in dichloromethane gives three characteristic IR absorption bands for the CO stretching vibration (Fig. 3a). Upon electrolysis of the solution, these three IR absorption bands

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\lambda_{	ext{max}}$(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(CO)$_3$COT</td>
<td>246 288 334 482</td>
</tr>
<tr>
<td>Mo(CO)$_3$COT</td>
<td>240 280 326 362 476</td>
</tr>
<tr>
<td>W(CO)$_3$COT</td>
<td>238 282 322 358 464</td>
</tr>
</tbody>
</table>

Table II. Electronic absorption spectral data of the complexes in n-hexane solution at room temperature.

![Fig. 2. Variation in the anodic current with the square root of voltage scan rate.](image)

![Fig. 3. FTIR spectrum of Cr(CO)$_3$(COT) in dichloromethane a) before electrolysis, b) after 8 h electrolysis at the first oxidation potential of 0.75 V versus Ag wire in dichloromethane.](image)
Fig. 4. ESR spectrum recorded during the electrolysis of Cr(CO)$_3$(COT) at the first oxidation potential of 0.75 V versus Ag wire in dichloromethane at -20°C.

gradually disappear, while a new feature concomitantly grows at 1980 cm$^{-1}$. The IR spectrum taken from the solution after 8 h of electrolysis (Fig. 3b) gives only one absorption band at 1980 cm$^{-1}$ which is readily assigned to hexacarbonylchromium(0).

From the experimental results it can be suggested that tricarbonyl($\eta^6$-cyclooctatetraene)metal(0) complexes undergo a stepwise two-electron oxidation yielding [M(CO)$_3$(\textit{$\eta^6$}-COT)]$^+$ and [M(CO)$_3$(\textit{$\eta^6$}-COT)]$^{2+}$, respectively. The latter species decomposes to yield M(CO)$_6$.

Since the electrolysis was carried out and followed by taking IR spectra at room temperature, no evidence for the intermediates was observed. However, when the electrolysis is carried out at the first oxidation potential and followed by recording ESR spectra at low temperature (e.g., -20°C) information can be obtained about intermediates. The ESR spectra recorded during the low temperature electrolysis show a singlet (g = 2.015, Fig. 4) which can be assigned to the 17-electron species, [Cr(CO)$_3$(\textit{$\eta^6$}-COT)]$^+$.

**Conclusion**

The tricarbonyl($\eta^6$-cyclooctatetraene)metal(0) complexes of group 6 elements were found to have an electrochemical behavior similar to that of hexacarbonylmetal(0) in dichloromethane solution at room temperature. The first oxidation peak potential of hexacarbonylmetal(0) increases on going from chromium to tungsten in line with the trend reported for the d-d transition energy (UV-Visible absorption spectra) and the first ionization energy (Photoelectron Spectroscopy) of the compounds. All these trends correlate very well with the decreasing HOMO energy level of the complexes by going from chromium to tungsten due to the increasing metal-ligand interaction. A similar trend is also observed for the tricarbonyl($\eta^6$-cyclooctatetraene)metal(0) complexes.

The first oxidation peak potentials of tricarbonyl($\eta^6$-cyclooctatetraene)metal(0) are found to be smaller than those of corresponding hexacarbonylmetals(0). This decrease in the first oxidation potential on passing from hexacarbonylmetal(0) to tricarbonyl($\eta^6$-cyclooctatetraene)metal(0) can be ascribed to the replacement of three facial carbonyl groups by cyclooctatetraene which has less $\sigma$-donating and $\pi$-accepting ability than carbon monoxide. As a result of this replacement the HOMO energy level of the complexes increases and their ionization energy decreases.

**Acknowledgement**

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