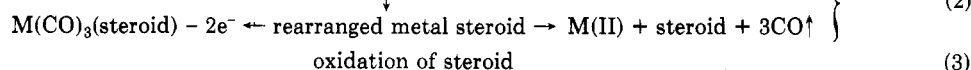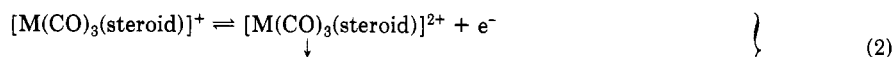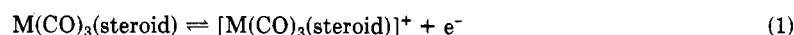# Electrochemical Oxidation of Hormonal Steroid Chromium, Molybdenum, and Tungsten Tricarbonyl Complexes in Dichloromethane

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The electrochemical oxidation of a series of tricarbonyl hormonal steroid complexes, M(CO)$_3$(steroid), (M = Cr, Mo, W; steroid = estrone 3-methyl ether, estrone, estradiol), has been examined in the noncoordinating solvent, dichloromethane. Three oxidation processes are observed at fast scan rates.

$$M(CO)_3(steroid) \rightleftharpoons [M(CO)_3(steroid)]^+ + e^- \qquad (1)$$

$$[M(CO)_3(steroid)]^+ \rightleftharpoons [M(CO)_3(steroid)]^{2+} + e^-$$
$$\downarrow$$
$$M(CO)_3(steroid) - 2e^- \leftarrow rearranged\ metal\ steroid \rightarrow M(II) + steroid + 3CO\uparrow \qquad (2)$$

$$oxidation\ of\ steroid \qquad (3)$$

As the scan rate is decreased, rearrangement of [M(CO)$_3$(steroid)]$^+$ occurs, and process 1 is transferred from a chemically reversible one-electron oxidation process into a chemically irreversible two-electron step. The rate of rearrangement of [M(CO)$_3$(steroid)]$^+$ is markedly dependent on the nature of the steroid. The stability order for [M(CO)$_3$(steroid)]$^+$ shows a well-defined trend: [Cr(CO)$_3$(steroid)]$^+$ $\gg$ [Mo(CO)$_3$(steroid)]$^+$ > [W(CO)$_3$(steroid)]$^+$. Controlled potential electrolysis experiments at potentials more positive than either process 1 or process 2 are consistent with a two-electron transfer. The uncomplexed steroid is recovered quantitatively in these experiments, without any evidence for rearrangement, and the overall oxidation process on the synthetic time scale is therefore M(CO)$_3$(steroid) $\rightarrow$ M(II) + 3CO$\uparrow$ + steroid + 2e$^-$. Chemical oxidation with NOPF$_6$ is also consistent with an oxidative elimination reaction generating free steroid. The mechanism proposed to account for the data is compared with those previously reported for arene complexes in coordinating solvents.

Introduction

The influence of transition metals in biological and enzymatic reactions has been studied widely for many years.[4] In particular, the binding of transition metals to enzymes, vitamins, and their precursors and to steroids has attracted considerable research.[5] Coordination to transition metals can also lead to useful synthetic methods. For example, it has been well-established that coordination of transition-metal moieties with steroids such as 3-keto-4-enes (reaction Scheme I) and conjugated dienes (reaction Scheme II) leads to functionalized and modified products which are difficult to synthesize by other means.[6–8]

It has been demonstrated that protection of a steroid diene by complexation with Fe(CO)$_3$ provides synthetic routes to novel steroids and vitamin precursors[9–11] via thermolytic and photochemical methods. Hormonal steroids can be coordinated to transition-metal carbo-
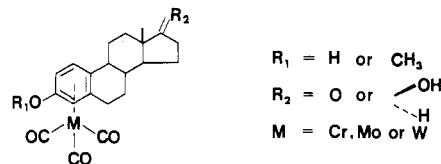
Scheme I

Scheme II

I

R$_1$ = H or CH$_3$

R$_2$ = O or $\stackrel{OH}{\underset{H}{\diagdown}}$

M = Cr, Mo or W
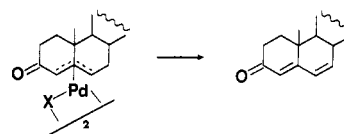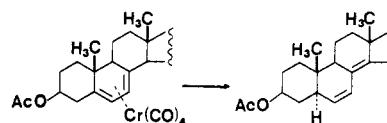
nyls[5,12,13] to produce M(CO)$_3$S (M = Cr, Mo, W; S = steroid) complexes of the kind shown in structure I. These complexes have been utilized advantageously in the field of analytical medical chemistry as new types of markers for endogenous steroids;[14,15] they have not been examined

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as routes for possible synthesis of new steroids.

Much interest has been shown in the area of inorganic electron-transfer reactions and catalysis (see ref 16–23, for example) as alternatives to thermolytic and photochemical synthetic routes. Electrochemical synthetic methods have also been successfully employed with noncoordinated steroids.[24] However, the redox properties of transition-metal hormonal steroids have yet to be reported, and whether the possibility of new electrochemical synthetic methods are available has yet to be established. In the present work the electrochemical and chemical oxidation of the tricarbonyl steroids $M(CO)_3(S)$ [where M = Cr, Mo, and W and S = estrone 3-methyl ether, estrone, and estradiol] has been studied. Of particular interest was to understand if eliminative oxidation of CO and steroid could be achieved and to ascertain if steroid modification occurs during the course of oxidation. Since the hormonal steroids investigated are steroid arene complexes, a comparison of results with electrochemical oxidation of simple arene complexes[25-38] also is considered in detail.

Experimental Section

Preparations. Preparation of $Cr(CO)_3(\eta^6\text{-estradiol})$.[39] 1,3,5(10)-Estratriene-3,17β-diol (0.55 g, 2.0 mmol) was dissolved in a mixture of n-butyl ether (90 mL) and tetrahydrofuran (10 mL). The solution was purged with dry, oxygen-free argon for 20 min and heated to 50 °C. To the solution was added hexacarbonylchromium (0.44 g, 2.0 mmol), and the reaction mixture was refluxed in an argon atmosphere for 48 h. The unreacted $Cr(CO)_6$ was sublimed, the solution filtered, and the filtrate evaporated to dryness in vacuo. In an inert atmosphere, the

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(39) (1,3,5(10)-estratriene-3,17β-diol)tricarbonylchromium is described in the text as $Cr(CO)_3(\text{estradiol})$. Other compounds have been described similarly by their trivial names.

Table I. Summary of Electrochemical Data for Oxidation of 1×10^{-3} M Hormonal Steroids at Platinum Electrodes in Dichloromethane at 20 °C[a]

compd	$(E_p^{ox.})$,[b] V vs. Ag/AgCl	$(E_{1/2})$,[c] V vs. Ag/AgCl
estradiol	+1.47	+1.49[d]
estrone	+1.56	+1.54
estrone 3-methyl ether	+1.73	+1.76

[a] $E^r_{1/2}$ for the $[Fe(C_5H_5)_2]^{+/0}$ redox couple is +0.495 V vs. Ag/AgCl in CH_2Cl_2. [b] $(E_p^{ox.})$ is the oxidation peak potential at stationary Pt electrode under conditions of cyclic voltammetry at a scan rate of 200 mV s^{-1}. Values are scan rate and concentration dependent. [c] $(E_{1/2})$ calculated from limiting current obtained at rotating platinum electrode at 2000 rpm. Values are rotation rate and concentration dependent. [d] No limiting current; $(E_{1/2})$ calculated from maximum current, see Figure 1a.

Table II. Summary of Cyclic Voltammetric Data for Oxidation of 1×10^{-3} M $Cr(CO)_3$(estrone 3-methyl ether) at a Platinum Electrode in Dichloromethane at 20 °C[a]

	scan rate, V·s^{-1}	$(E_p^{ox.})$, V vs. Ag/AgCl	$(E_p^{red.})$, V vs. Ag/AgCl	$E^r_{1/2}$, V vs. Ag/AgCl
process 1	0.200	+0.77	b	c
	0.500	+0.79	b	c
	1.00	+0.80	b	c
	5.00	+0.82	+0.67	0.75
	10.0	+0.85	+0.65	0.75
	50.0	+0.90	+0.55	0.73
process 2	0.200	+1.20	b	c
process 3	0.200	+1.70	b	c

[a] Values of $E^r_{1/2}$ for $[Fe(C_5H_5)_2]^{+/0}$ redox couple is +0.495 V vs. Ag/AgCl in CH_2Cl_2. $E_p^{ox.}$ and $E_p^{red.}$ are the oxidation and reduction peak potentials at given scan rate, respectively. $E^r_{1/2}$ = reversible half-wave potential calculated as the average of $E_p^{ox.}$ and $E_p^{red.}$. [b] No reduction peak. [c] Not applicable.

remaining solid residue was taken up in a minimum quantity of diethyl ether and filtered. The procedure was replicated until the clear yellow solution on cooling (acetone/CO_2 bath) afforded yellow air-sensitive crystals of $Cr(CO)_3(\eta^6\text{-estradiol})$: yield 0.3 g (37%); mp 127 °C dec (lit.[13] 125 °C dec); IR ($\nu(CO)$, CH_2Cl_2) 1955 (s), 1873 (br) cm^{-1} (lit.[13] 1955, 1875 cm^{-1}); MS, m/e 408.5 (calcd 408.4).

Preparation of Other Compounds. Other $M(CO)_3(\text{steroid})$[39] compounds were prepared and characterized according to literature procedures[13] and stored in a nitrogen/vacuum atmosphere glovebox.

Chemicals and Reagents. Steroids were obtained from the Sigma Chemical Co., metal hexacarbonyls from Strem Chemicals, and tetrabutylammonium perchlorate from Southwestern Analytical Chemicals. These materials were all vacuum dried before use. Carbon monoxide from CIG, Australia, was used as received.

Instrumentation. IR spectra were recorded with a Perkin-Elmer 457 spectrophotometer (calibrated against polystyrene). Mass spectra were obtained with a Finnigan 3200 series mass spectrometer.

Voltammograms were recorded in dichloromethane (0.1 M Bu_4NClO_4) by using either a BAS CV-27 voltammograph coupled with a Houston Instruments Model 100 X-Y Recorder or a BAS-100 electrochemical analyzer employing a conventional three-electrode cell at (20 ± 1) °C. For cyclic voltammetry, the working electrode was a BAS platinum disk electrode, while for rotating electrode voltammetry, Metrohm or Beckmann rotating platinum disk electrodes and electrode assemblies were used. The reference electrode was Ag/AgCl (saturated LiCl, CH_2Cl_2) and the auxiliary electrode was a platinum wire. Solutions of steroid metal carbonyls for electrochemical measurements were prepared just before use, degassed with argon, and maintained under an argon atmosphere throughout the measurements. Oxidation of 10^{-3} M ferrocene was routinely used for calibration purposes.

A PAR Model 173 potentiostat/galvanostat was used for the controlled potential electrolysis experiments with a platinum gauze working electrode, Ag/AgCl reference electrode, and a platinum gauze auxiliary electrode separated from the bulk solution via a
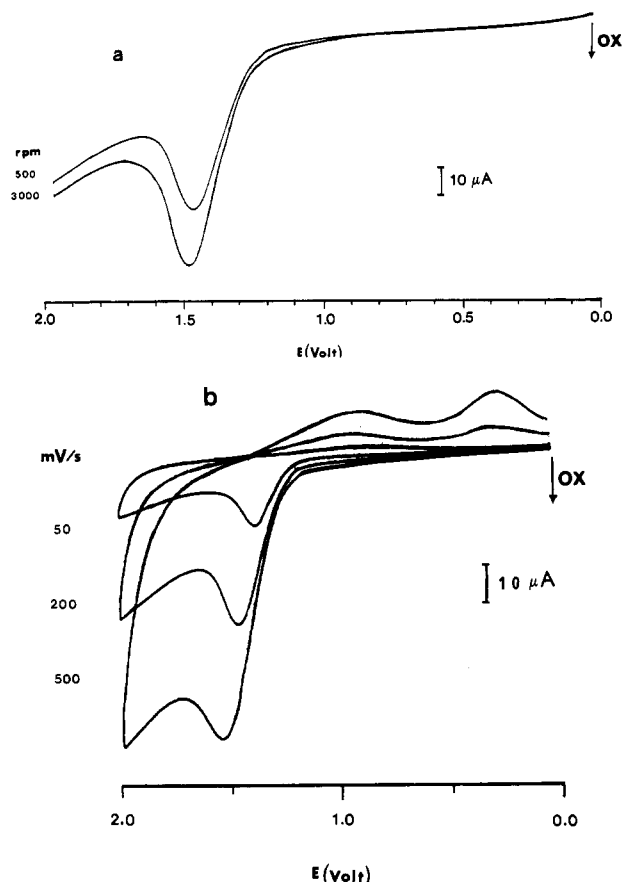
Figure 1. Voltammograms for the oxidation of 1 × 10⁻³ M estradiol in CH_2Cl_2 (0.1 M Bu_4NClO_4) at (a) a stationary platinum electrode and (b) a rotating platinum disk electrode.

Figure 2. Voltammograms of 1 × 10⁻³ M $Cr(CO)_3$(estrone 3-methyl ether) in CH_2Cl_2 (0.1 M Bu_4NClO_4) obtained at a rotating platinum disk electrode.
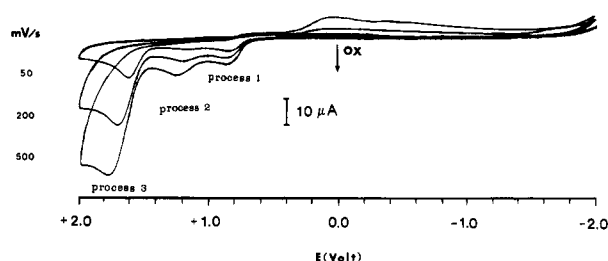
Figure 3. Cyclic voltammograms for the oxidation of 1 × 10⁻³ M $Cr(CO)_3$(estrone 3-methyl ether) in CH_2Cl_2 (0.1 M Bu_4NClO_4) obtained at a stationary platinum electrode. Initial potential is 0.00 V vs. Ag/AgCl.

salt bridge containing a porous vycor plug. Coulometric determinations were undertaken with the aid of a PAR Model 179 digital coulometer.

Chromatograms were obtained under HPLC conditions by using a Millipore-Waters M45 pump, Model 440 UV detector at λ = 254 nm, and Merck 125 mm × 4 mm Lichrosorb RP-18 column. The mobile phase was 70:30 methanol/water buffered with 0.01 M $(NH_4)_2HPO_4$ for $Cr(CO)_3$(estrone 3-methyl ether) and 55:45 methanol/water with 0.01 M $(NH_4)_2HPO_4$ for $Cr(CO)_3$(estrane). The mobile phase flow rate was 2.0 mL·min⁻¹.

Results and Discussion

Electrochemical Oxidation of Free Steroids. The electrochemical activity of hormonal steroids has been studied.[40-45] Estrogens are oxidized at fairly positive potentials.[46] The electrochemical responses of the free steroids are an important factor in elucidating the electrochemical oxidative mechanism of metallic carbonyl steroid complexes and are therefore briefly reported. Figure 1a shows the rotating electrode and Figure 1b cyclic voltammograms of the electrochemical oxidation of estradiol. The oxidation current is a linear function of
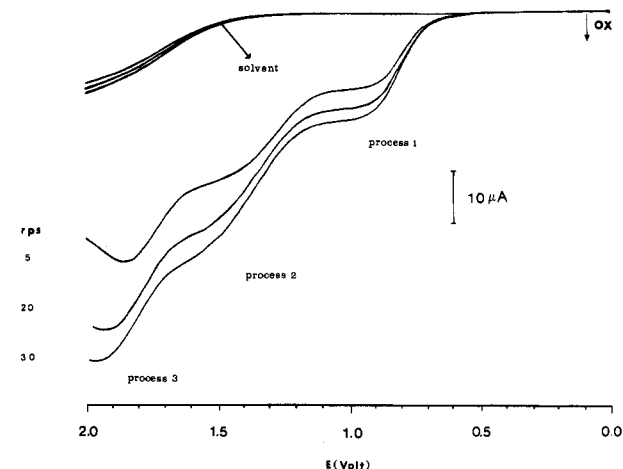
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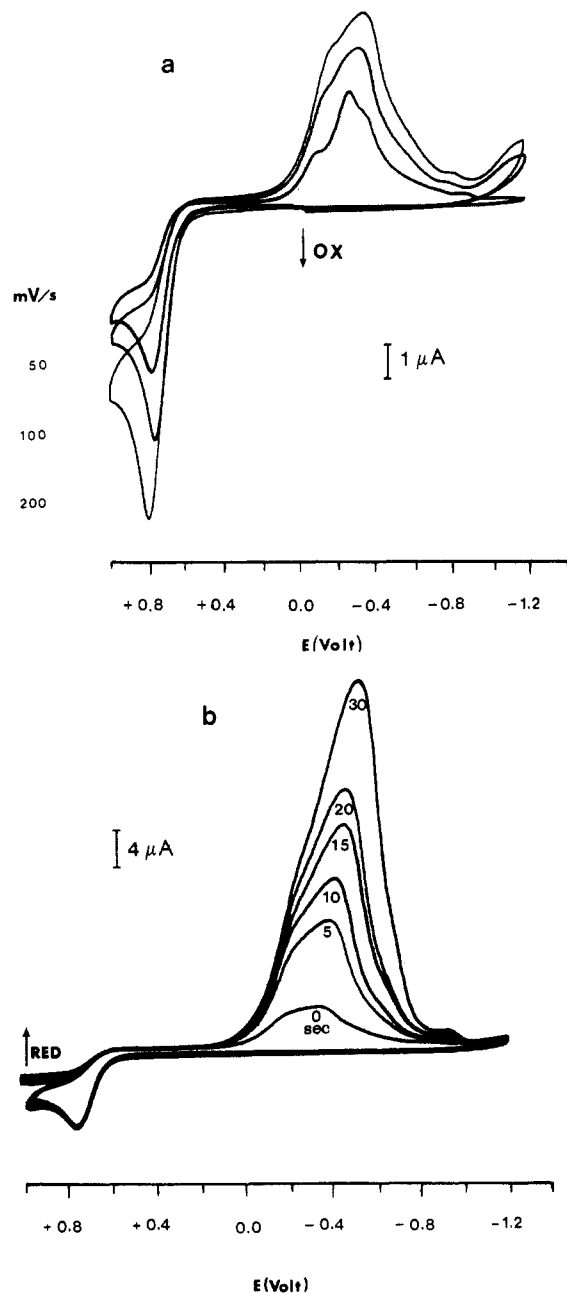(46) Shihaki, Z. K.; Scaro, J.; Thomas, B. F. *J. Chromatogr.* **1981**, *22*, 99.

concentration. On the reverse scan of this oxidative cyclic voltammogram well-defined peaks consistent with product adsorption or stripping of insoluble materials are observed. The height of the peaks on the reverse scan is a function of the time the potential is held beyond the oxidation peak. The electrochemical data for the estrogens are summarized in Table I.

Electrochemical Oxidation of $Cr(CO)_3$(estrone 3-methyl ether). Figure 2 shows voltammograms obtained in CH_2Cl_2 at a rotating platinum disk electrode. Three processes are observed each with a designated number as given in Figure 2. Process 3 near the solvent limit can be assigned to the oxidation of steroid. Processes 1 and 2 have limiting currents of similar magnitude to each other (after background correction).

Cyclic voltammograms in Figure 3 exhibit some interesting comparisons with the rotating electrode voltammograms. Three processes are observed, as was the case at the rotating electrode. However, at low scan rates, process 2 is almost unobservable. As the scan rate increases, process 2 becomes well-defined. At scan rates in excess of approximately 200 mV s⁻¹, both waves are of similar height. Process 3, attributed to oxidation of the steroid, is present for all scan rates.

Figure 4a illustrates the effect in cyclic voltammetry when the potential is switched between process 1 and process 2 at various scan rates. Figure 4b shows the response when the potential when the potential is held at +1.00 V for varying time intervals. On the reverse scan after holding the potential at positive potentials a large peak is observed which demonstrates characteristics of an adsorbed or insoluble product attaching itself to the electrode surface. At very fast scan rates (Figure 5), process 1 is chemically reversible and the surface process

Figure 5. Cyclic voltammograms showing the first oxidation process of 1×10^{-3} M Cr(CO)$_3$(estrone 3-methyl ether) in CH$_2$Cl$_2$ (0.1 M Bu$_4$NClO$_4$) when a stationary platinum electrode at fast scan rates and an initial potential of 0.10 V vs. Ag/AgCl are used.

Figure 6. Cyclic voltammograms showing the first two oxidation processes of 1×10^{-3} M Cr(CO)$_3$(estrone 3-methyl ether) in CH$_2$Cl$_2$ (0.1 M Bu$_4$NClO$_4$) when a stationary platinum electrode and an initial potential of 0.10 V vs. Ag/AgCl are used.

Figure 4. Cyclic voltammograms of 1×10^{-3} M Cr(CO)$_3$(estrone 3-methyl ether) in CH$_2$Cl$_2$ (0.1 M Bu$_4$NClO$_4$) obtained at a stationary platinum electrode: (a) potential switched at +1.00 V vs. Ag/AgCl after commencing scan at 0.00 V vs. Ag/AgCl and (b) initial potential held at +1.00 V vs. Ag/AgCl at time intervals indicated.

Figure 7. Chromatograms of (a) 10 μL (10 nmol) of 10^{-3} M Cr(CO)$_3$(estrone 3-methyl ether) [sens. 0.10], (b) 25 μL 10^{-3} M (25 nmol) of electrolyzed Cr(CO)$_3$(estrone 3-methyl ether) [sens. 0.02], and (c) 25 μL (25 nmol) of 10^{-3} M estrone 3-methyl ether) [sens. 0.02] at a mobile phase flow rate of 2 mL·min^{-1}. Retention times (t_R): t_R(complex) = 4.2 min; t_R(steroid) = 8.0 min.

on the reverse scan is absent. Importantly, the position of this response at –0.4 V vs. Ag/AgCl is well-removed from the material produced by oxidation of free steroid, thereby eliminating the possibility of a catalytic ligand based oxidation process being operative.

Figure 6 indicates that the second process is not chemically reversible even at very fast scan rates. However, for scan rates greater than 1 V·s^{-1}, a reduction process is evident in the vicinity of –0.4 V which has exactly the same characteristics as that observed when the potential is held between process 1 and process 2 for short periods of time. Processes 1 and 2 are independent of carbon monoxide concentration in solution (added at partial pressures up to 1 atm) and steroid concentration (1×10^{-4} to 1×10^{-2}M).

Figure 7 shows chromatograms before and after controlled potential electrolysis at 1.0 V vs. Ag/AgCl in CH$_2$Cl$_2$
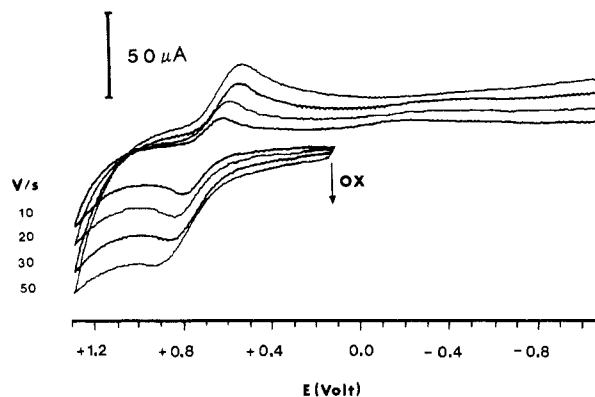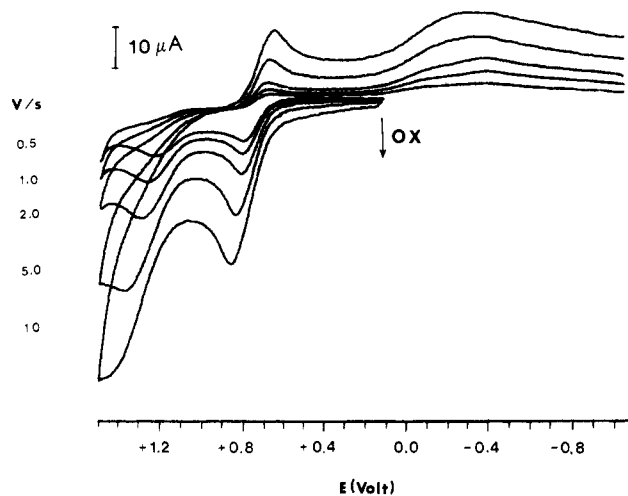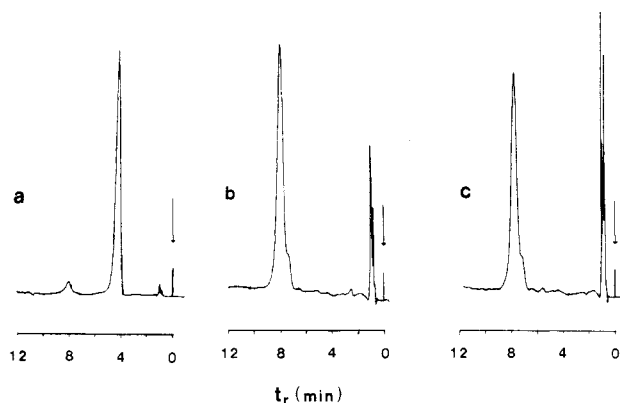
at 20 °C. Quantitatively, the free steroid is recovered at the (95 ± 5)% level irrespective of whether the applied potential is more positive than either the first or the second process. The infrared spectrum after electrolysis shows the complete absence of metal carbonyl bands, but all steroid bands remain. The infrared data in conjunction with HPLC data imply oxidative elimination of the car-

Table III. Summary of Cyclic Voltammetric Data for Oxidation of 1×10^{-3} M Steroid Hormonal Chromium, Molybdenum, and Tungsten Tricarbonyl Complexes at a Platinum Electrode in Dichloromethane at 20 °C[a]

|	process 1[b]			process 2[c]	process 3[b]
compd	$(E_p{}^{ox.})_1$,[c] V vs. Ag/AgCl	$(E_p{}^{red.})_1$,[c] V vs. Ag/AgCl	$(E^r{}_{1/2})_1$,[c] V vs. Ag/AgCl	$(E_p{}^{ox.})_2$, V vs. Ag/AgCl	$(E_p{}^{ox.})_3$, V vs. Ag/AgCl
Cr(CO)₃(estrone 3-methyl ether)	+0.77	d	d	+1.20	+1.70
Cr(CO)₃(estrone)	+0.75	+0.65	+0.70	+1.21	+1.60
Cr(CO)₃(estradiol)	+0.73	+0.63	+0.68	+1.28	+1.50
Mo(CO)₃(estradiol)	+0.70	d	d	+1.04	+1.44
W(CO)₃(estradiol)	+0.75	d	d	+1.18	+1.40

[a] $E^r{}_{1/2}$ for $[Fe(C_5H_5)_2]^{+/0}$ redox couple is +0.495 V vs. Ag/AgCl in CH_2Cl_2. $(E_p{}^{ox.})_n$ is the oxidation peak potential and $(E_p{}^{red.})_n$ is the reduction peak potential for process n (n = 1–3). $(E^r{}_{1/2})_1$ is the reversible half-wave potential calculated as the average of $(E_p{}^{ox.})_1$ and $(E_p{}^{red.})_1$. [b] Data obtained under conditions of cyclic voltammetry at a scan rate of 200 mV·s⁻¹. [c] Data obtained under conditions of cyclic voltammetry at a scan rate of 10 V·s⁻¹. [d] No reduction peak.

bonyl steroid occurs at potentials positive of either process 1 or process 2. Electrochemical monitoring of controlled potential electrolysis experiments reveals the disappearance of the carbonyl complex (processes 1 and 2 vanish) while the response due to the noncoordinated steroid remains. Mass spectrometry also confirmed the generation of free steroid after electrolysis. Coulometric data gave an n value of 1.95 ± 0.05 electrons in the charge-transfer process irrespective of whether the potential was applied at potentials more positive than either process 1 or process 2. Chemical oxidation with $NOPF_6$ also led to the oxidation of $Cr(CO)_3$(steroid) with identical products produced as in the case of controlled potential electrolysis experiment.

Rotating disk electrode experiments showed that the limiting current per unit concentration of the known one-electron oxidation reaction of the tricarbonyl complex $fac\text{-}Cr(CO)_3(P(OMe)_3)_3{}^{47}$ to be essentially identical with process 1 of $Cr(CO)_3$(steroid) at fast scan rates or fast electrode rotation rates. At slow scan rates, process 1 appears to involve transfer of more than one electron and process 2 less than one, but the sum is always equal to two electrons. This and other data are consistent with processes 1 and 2 both being one-electron steps at short time domains. Process 1 under short time scale experiments is assigned to reaction 1. On the long time scale of con-

$$Cr(CO)_3(\text{steroid}) \rightleftharpoons [Cr(CO)_3(\text{steroid})]^+ + e^- \quad (1)$$
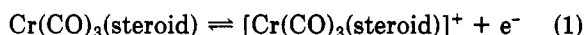
trolled potential electrolysis (or chemical oxidation) it is clear that the process is a two-electron step. Furthermore, the same products are obtained irrespective of whether the oxidation potential is positive of process 1 or 2 or if chemical oxidation is employed. This is consistent with the concept that $[Cr(CO)_3(\text{steroid})]^+$ is inherently unstable on long time scale experiments and rearranges to give an ECE-type mechanism. The overall oxidation process is given in eq 2. Voltammetric data reveal that the same

$$Cr(CO)_3(\text{steroid}) \rightarrow Cr(II) + \text{steroid} + 3CO\uparrow + 2e^- \quad (2)$$
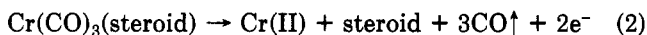
intermediate chromium complex is formed after the potential was held between process 1 and process 2 or the data scanned through for the two-electron stage as evidenced by well-defined reduction waves at –0.4 V on the reverse scan of cyclic voltammograms. This species is not oxidized ligand and appears to be an adsorbed or precipitated two-electron-oxidized product of $Cr(CO)_3$(steroid). Clearly, this surface active species is not stable on the synthetic time scale and ultimately decomposes to produce free steroid and carbon monoxide.

Electrochemical Oxidation of $Cr(CO)_3$(estrone). Process 1 in this case is chemically reversible even at slow
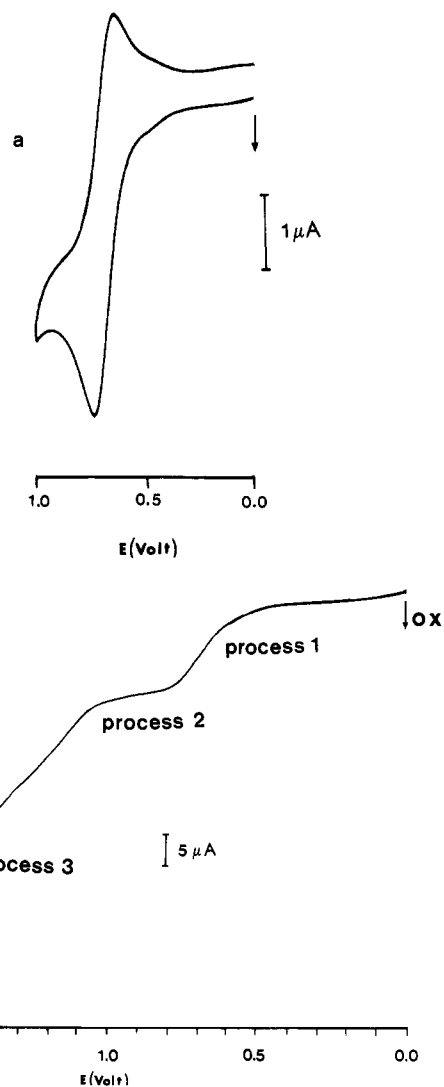
(47) Bond, A. M.; Carr, S. W.; Colton, R. *Organometallics* 1984, 3, 541.

Figure 8. Voltammograms for the oxidation of 1×10^{-3} M $Cr(CO)_3$(estrone) in CH_2Cl_2 (0.1 M Bu_4NClO_4): (a) cyclic voltammogram of process 1 when a stationary platinum electrode at a scan rate of 200 mV·s⁻¹ is used; (b) voltammogram of processes 1, 2, and 3 at a rotating platinum disk electrode at 500 rpm.

scan rates so that $[Cr(CO)_3(\text{estrone})]^+$ is apparently more stable than $[Cr(CO)_3(\text{estrone 3-methyl ether})]^+$. The experimental data are summarized in Table III and parallel that for $Cr(CO)_3$(estrone 3-methyl ether) at fast scan rates. That is, mechanistic details for the two carbonyl steroids are believed to be similar, but reaction rates for decomposition of $[Cr(CO)_3(\text{steroid})]^+$ are faster in the case of the estrone 3-methyl ether complex.

Controlled potential electrolysis at potential after the first or second process gave an n value of 1.91 ± 0.05

electrons in the charge-transfer process. After electrolysis, the steroid was recovered quantitatively, as demonstrated by HPLC, infrared, and electrochemical monitoring. No metal carbonyl IR bands were observed after bulk electrolysis of the complex. $NOPF_6$ oxidation of $Cr(CO)_3$(estrone) gave the same products as for electrochemical oxidation.

The observed reaction on the synthetic time scale is eq 3. This indicates that the overall process is essentially identical with $Cr(CO)_3$(estrone 3-methyl ether), despite the evidence for enhanced stability of $[Cr(CO)_3(estrone)]^+$ on the voltammetric time scale.

$$Cr(CO)_3(estrone) \rightarrow Cr(II) + (estrone) + 3CO\uparrow + 2e^- \quad (3)$$
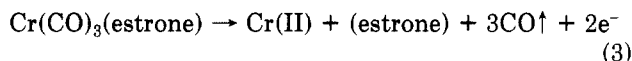
Electrochemical Oxidation of $Cr(CO)_3$(estradiol). $Cr(CO)_3$(estradiol) was found to be the most stable of the 18-electron steroid complexes in CH_2Cl_2. Two well-defined one-electron oxidation processes are observed in addition to process 3 assigned to the oxidation of estradiol. Experimental data are summarized in Table III. The first process is chemically reversible under all voltammetric conditions examined, and it was hoped that isolation of a stable 17-electron species $[Cr(CO)_3estradiol]^+$ may have been possible. However, controlled potential electrolysis or chemical oxidation with $NOPF_6$ is again consistent with an overall two-electron oxidation (eq 4).
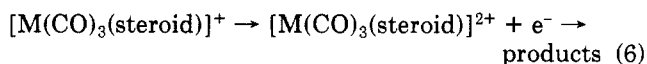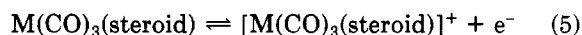
$$Cr(CO)_3(estradiol) \rightarrow$$
$$Cr(II) + (estradiol) + 3CO\uparrow + 2e^- \quad (4)$$
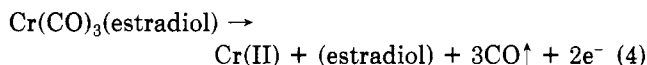
Electrochemical Oxidation of $M(CO)_3$(estradiol) (M = Mo, W). These starting materials are much more reactive than their chromium analogues, and this feature is transferred to the oxidized complexes. Thus the electrochemical behavior of the Mo estradiol complex resembles that of $Cr(CO)_3$(estrone 3-methyl ether). That is, process 1 exhibits chemical reversibility at fast scan rates. As the scan rate is increased, process 2 increases in magnitude and is well-defined under conditions where process 1 is reversible. With the W complexes, process 2 is extremely small relative to process 1 for most scan rates examined. The limiting current at slow scan rates for the irreversible present is approximately twice that for the reversible one-electron oxidation of the chromium complexes. Only with scan rates of 50 $V \cdot s^{-1}$ is partial reversibility seen for process 1. Data for the Cr, Mo, and W complexes are compared in Table III.

There is a well-defined stability trend exhibited with the oxidized estradiol complexes:

$$[Cr(CO)_3(estradiol)]^+ \gg [Mo(CO)_3(estradiol)]^+ >$$
$$[W(CO)_3(estradiol)]^+$$
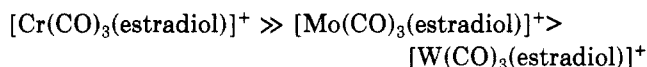
Mechanistic Considerations. All data suggest that a similar electrochemical mechanism is operative for all complexes, irrespective of metal or steroid. However the kinetic stability of the different 17-electron cations appears to be vastly different. For all of the complexes, two one-electron transfer steps are observed at very fast scan rates (e.g., 50 $V \cdot s^{-1}$). The first process (eq 5) at fast scan rates corresponds to the generation of a 17-electron cation. The second oxidative step corresponds to process 6. On longer

$$M(CO)_3(steroid) \rightleftharpoons [M(CO)_3(steroid)]^+ + e^- \quad (5)$$

$$[M(CO)_3(steroid)]^+ \rightarrow [M(CO)_3(steroid)]^{2+} + e^- \rightarrow \text{products} \quad (6)$$

time scale controlled potential electrolysis experiments a

Scheme III
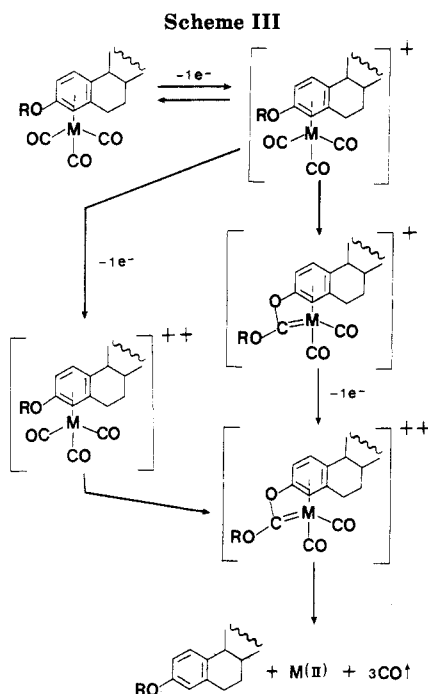
single two-electron process (eq 7) is observed, irrespective of the oxidation potential.

$$M(CO)_3(steroid) \rightarrow M(II) + 3CO\uparrow + steroid + 2e^- \quad (7)$$
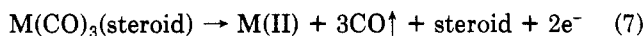
Cyclic voltammetric data indicate that an intermediate is present prior to the ultimate elimination of steroid, which is recovered quantitatively in an unmodified form. Stability comparisons of the steroid complexes when bonded to $Cr(CO)_3$ show greater reactivity for the decomposition of the cation $[Cr(CO)_3(steroid)]^+$ when an $-OCH_3$ group is attached to the arene ring of the steroid rather than is the case with an $-OH$ group. Similarly, greater reactivity is found when Mo or W replaced Cr in the series of $[M(CO)_3(steroid)]^+$ complexes.

A rationalization for the high reactivity and nature of the intermediate can be presented. The stereochemistry of the tridentate ligand steroid in the metal carbonyl complex forces the carbonyl groups into a facial geometry. It has been shown experimentally[47,48] that this configuration is electronically strained for a 17-electron group 6 carbonyl compound. That is, a meridional configuration would have a lower energy. However, clearly a meridional geometry is impossible for the $[M(CO)_3(steroid)]^+$. It is postulated that an alternative rearrangement occurs to relieve the electronic strain. It is possible to achieve an alternative geometry via migration of a proton or methyl group from the arene steroid ring.[25] This species is expected to be readily oxidized to a formally 18-electron oxidation state (II) species which are common in group 6 carbonyl chemistry.[49-53] For example,[50] electrochemical oxidation of $M(CO)_3(\eta^1\text{-dpm})(\eta^2\text{-dpm})$ leads to formation of the 18-electron, seven-coordinate species $[M(CO)_3(\eta^2\text{-dpm}_2)]^{2+}$ where dpm = bis(diphenylphosphino)methane.

(48) Bond, A. M.; Darensbourg, D. J.; Mocellin, E.; Stewart, B. J. *J. Am. Chem. Soc.* **1981**, *103*, 6827.

(49) Panizo, M.; Cano, M. *J. Organomet. Chem.* **1985**, *287*, 221.

(50) Bond, A. M.; Colton, R.; McGregor, K. *Inorg. Chem.* **1986**, *25*, 1880 and references cited therein.

(51) Brown, L. D.; Datta, S.; Kouba, J. K.; Smith, L. K.; Wreford, S. S. *Inorg. Chem.* **1978**, *17*, 729.

(52) Datta, S.; Wreford, S. S. *Inorg. Chem.* **1977**, *16*, 1134.

(53) Fong, L. K.; Fox, J. R.; Foxman, B. M.; Cooper, N. *J. Inorg. Chem.* **1986**, *25*, 1880.

A common reduction process at negative potentials is observed on the reverse scan of cyclic voltammetry either after a two-electron oxidation or under conditions where process 1 is an ECE-type mechanism. This process presumably corresponds to a two-electron reduction of a rearranged seven-coordinate oxidation state(II) complex to $M(CO)_3$(steroid).

Reaction Scheme III demonstrates a proposed mechanism for a process involving formation of a rearranged steroid with two competing pathways. Quantitative recovery of the initial steroid and not a modified steroid is observed experimentally and would be expected by the proposed mechanism when the 18-electron oxidation state (II) complex decomposes.

A number of mechanistic pathways for the oxidation of arene metal carbonyls complexes have been reported. In noncoordinating solvents, Lloyd et al.[29] observed two one-electron steps. The first process was reversible and the second irreversible. The potential separating the two processes was approximately 1 V. In our work, the difference in potential between the two oxidation processes is about 0.5 V. However, generally results for the hormonal steroids parallel those of electrochemical studies of related arene complexes in dichloromethane.

In other reports,[26,27,33–37] coordinating solvents such as acetonitrile and dimethylformamide have been used. Frequently, irreversible waves were observed in such media

and the total number of electrons associated with the oxidation process seems to vary between two and three. In the presence of coordinating ligands, alternative pathways are available for releasing the electronic strain. E.g., formation of a 19-electron intermediate by direct addition of a ligand[25] or formation of a metal carbonyl complex with loss of arene.[33–37] These solvent-assisted pathways are not available in a noncoordinating solvent, such as dichloromethane, and cannot be considered in the present work. However, clearly the mechanism proposed is a form of a 19-electron intermediate achieved via an internal rearrangement and in this sense bears some resemblance to the mechanism proposed by Doxsee, Grubbs, and Anson[25] to explain reactivity in the presence of coordinating ligands.

Registry No. Estradiol, 50-28-2; estrone, 53-16-7; estrone 3-methyl ether, 1624-62-0; $Cr(CO)_3$ (estradiol), 77109-92-3; $Cr(CO)_3$ (estrone 3-methyl ether), 12171-88-9; $Cr(CO)_3$ (estrone), 12243-26-4; $Mo(CO)_3$ (estradiol), 77089-95-3; $W(CO)_3$ (estradiol), 77089-96-4.

Photochemical Reaction of Fe(CO)₂(NO)₂ and Co(CO)₃NO with 1,3-Butadiene in Liquid Xenon Solution: Possible Intermediates in the Catalytic Dimerization of Dienes

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IR spectroscopic evidence is presented showing that UV photolysis of $Co(CO)_3NO$ and $Fe(CO)_2(NO)_2$ in liquid Xe (LXe) doped with 1,3-butadiene (C_4H_6) yields η^2-C_4H_6 and η^4-C_4H_6 complexes of Co (1 and 2) and Fe (3–5). Under similar photolytic conditions in liquid Kr, $Ni(CO)_4$ forms only $Ni(CO)_3(\eta^2$-$C_4H_6)$, which is thermally less stable than the compounds of Fe and Co. Both $Co(CO)_2(NO)(\eta^2$-$C_4H_6)$ (1) and $Fe(CO)(NO)_2(\eta^2$-$C_4H_6)$ (3) are thermally stable up to –35 °C in LXe. $Co(CO)(NO)(\eta^4$-$C_4H_6)$ (2) reacts thermally with CO to regenerate 1 with an enthalpy of activation $6 < \Delta H^* < 15$ kcal mol^{-1} and a half-life of ~11 min at –41 °C. $Fe(NO)_2(\eta^4$-$C_4H_6)$ (5) has a similar thermal stability. Only $Fe(CO)_2(NO)_2$, a known catalyst for photodimerization of butadiene, forms a bis(butadiene) complex, $Fe(NO)_2(\eta^2$-$C_4H_6)_2$ (4), which is a likely candidate for the catalytically active intermediate. We suggest that catalysis may proceed via a five-coordinate intermediate $Fe(NO)_2(\eta^2$-$C_4H_6)(\eta^4$-$C_4H_6)$ (8) with a bent NO group. Species 1 through 5 have been characterized by observation of IR bands due not only to $\nu(CO)$ and $\nu(NO)$ but also to coordinated C_4H_6. Tentative assignments of these C_4H_6 spectra are given.

Introduction

It has been known for many years that transition-metal nitrosyl compounds can photocatalyze the dimerization of dienes.[1–3] Particularly striking is the contrast between

$Fe(CO)_2(NO)_2$, a highly specific catalyst for the dimerization of butadiene to 4-vinylcyclohexene,[2] and $Co(CO)_3NO$, which is catalytically almost inactive.[2] A number of detailed studies have together shown that "$Fe(NO)_2$" is the active catalyst. Carbon monoxide suppresses catalysis[1,2] while "$Fe(NO)_2$" precursors such as $[Fe(NO)_2Cl]_2$ can be used to generate catalysts.[4] Furthermore, Fe-

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(3) Lombardo, L.; Wege, D.; Wilkinson, S. P. *Aust. J. Chem.* 1974, 27, 143. Moggi, L.; Juris, A.; Sandrini, D.; Manfrin, M. F. *Rev. Chem. Intermed.* 1981, 4, 171.

(4) Ballivet, D.; Billard, C.; Tkatchenko, I. *Inorg. Chim. Acta* 1977, 25, L58. Ballivet-Tkatchenko, D.; Riveccie, M.; El Murr, N. *Ibid.* 1978, 30, L289; *J. Am. Chem. Soc.* 1979, 101, 2764.