Contribution from the Department of Inorganic Chemistry,
University of Melbourne, Parkville, 3052, Victoria, Australia

Electrochemical Investigations of the Group VI Halopentacarbonylmetalate(0) Complexes

A. M. BOND,* J. A. BOWDEN, and R. COLTON

Received July 26, 1973

Chemical oxidation of the $[Cr(CO)_5I]^-$ anion with iodine is known to produce the complex $Cr(CO)_5I$, and no higher oxidation state halocarbonyl species of chromium are known. On the other hand, halogenation of $[M(CO)_5X]^-$ (M = Mo and W; X = Br and I) leads to the metal(II) species $[M(CO)_4X_3]^-$, without the formation of intermediate metal(I) complexes. Thus, an apparent difference between group VI metals has been indicated in the literature. Electrochemical oxidation is considerably more specific than chemical oxidation and can lead to detailed thermodynamic and kinetic information on the oxidation pathways. The use of linear sweep dc, cyclic, ac, and pulse voltammetry at platinum, glassy carbon, and dropping mercury electrodes has therefore been used in an electrochemical investigation of the $[M(CO)_5X]^-$ (M = Cr, Mo, and W; X = Cl, Br, and I) series of complexes in acetone. With chromium, two one-electron oxidation steps are observed. The first oxidation is a reversible one-electron step

$$[Cr(CO)_5X]^- \overset{e^-}{\rightleftharpoons} Cr(CO)_5X$$

and at room temperature the second step is

$$Cr(CO)_5X \overset{e^-}{\rightleftharpoons} [Cr(CO)_5X]^+ \xrightarrow{k} \text{products}$$

The use of low-temperature electrochemistry reveals that the chromium(II) cation is stable at −75° and substantiates the postulation of hitherto unknown chromium(II) halocarbonyls. By contrast with Cr, the $M(CO)_5X$ (M = Mo and W) complexes possess no inherent stability and appear to either disproportionate or rearrange or react giving rise to an ECE mechanism. With either mechanism a metal(II) species is the end product. Data are consistent with reported chemical oxidations and results indicate possible synthetic pathways to a number of new group VI metal halocarbonyls.

Introduction

The *chemical* oxidation of the halopentacarbonylmetalate(0) anions, $[M(CO)_5X]^-$ (M = Cr, Mo, and W; X = Cl, Br, and I), has been investigated by a number of workers. In 1961, Behrens and Zilsperger[1] reported the formation of $Cr(CO)_5I$ by iodine oxidation of $[Cr(CO)_5I]^-$ and this was later confirmed by King[2] who found, however, that the analogous reactions for molybdenum and tungsten produced the triiodotetracarbonylmetalate(II) anions, $[M(CO)_4I_3]^-$ (M = Mo and W). No metal(I) complex was observed in these cases. These reactions, and analogous ones of $[M(CO)_5Br]^-$ with bromine, were later examined by Ganorkar and Stiddard,[3] and similar derivatives were produced. These same products, as well as their chloro analogs, were subsequently prepared[4] by reaction of the appropriate halide salt with the halocarbonyls[5] $[M(CO)_4X_2]_2$.

Until now, there has been no evidence for the existence of any Mo(I), W(I), or Cr(II) halocarbonyls. In fact, the only other chromium halocarbonyls reported[6,7] are $Cr_2(CO)_{10}I$ and $[Cr_2(CO)_{10}I]^-$ involving formal oxidation states for chromium of (0) to (I). Some mixed $[MM'(CO)_{10}X]^-$ (M = M′ = Cr, Mo, and W) were also reported.[7]

From the above, it appears that chemical oxidation of the $[M(CO)_5X]^-$ anions varies considerably with metal. Electrochemical oxidation, being more specific, has been applied to this system in an attempt to explain these apparent differences. The electrochemical techniques of cyclic, linear sweep, pulse, and ac voltammetry at both Pt and Hg electrodes over a temperature range from −75 to +20° in acetone have enabled the identification of some new species in solution and a systematic explanation of previously reported chemical oxidations.

Experimental Section

Reagents. All chemicals used were of reagent or spectroscopic grade purity.

Compounds. All $[M(CO)_5X]^-$ anions were isolated as their tetraethylammonium salts and were prepared by the method of Abel, *et al.*[8]

Instrumentation. All voltammograms and polarograms were recorded with PAR Electrochemistry System Model 170 (Princeton, N. J.). A three-electrode format with positive feedback circuitry was used in all cases. Linear sweep and cyclic voltammograms were recorded with scan rates of up to 200 mV/sec. Fundamental and second harmonic ac voltammograms were recorded with phase-sensitive detection using an alternating potential of 10 mV p-p at frequencies between 10 and 1100 Hz. Pulse polarograms were recorded using a sampling duration of 15 msec at 1-sec intervals. Further details of operating conditions are given in the tables and at appropriate places in the text and figures.

Electrodes and Other Electrochemical Apparatus and Techniques. The supporting electrolyte used was 0.1 *M* tetraethylammonium perchlorate in all cases except for low-temperature work where a saturated solution was used. All solutions were degassed with argon. The low-temperature electrochemistry was performed using water–ice (0°) and Dry Ice–acetone (−75°) thermostating. Otherwise, solutions were thermostated at 20°.

Working electrodes used were Pt wire, Pt foil, glassy carbon, dropping mercury electrode, and hanging drop mercury electrodes (Metrohm BM-503). Short controlled drop time (0.16 sec) dc polarograms were obtained using Metrohm Polarographie Stand E354. The auxiliary electrode used was Pt wire or foil and the reference electrode Ag–AgCl (0.1 *M* LiCl, acetone) was separated from the test solution by a salt bridge containing 0.1 *M* tetraethylammonium perchlorate.

---

[1] H. Behrens and H. Zilsperger, *Z. Naturforsch. B*, 16, 349 (1961).

[2] R. B. King, *Inorg. Chem.*, 3, 1039 (1964).

[3] M. C. Ganorkar and M. H. B. Stiddard, *J. Chem. Soc.*, 3494 (1965).

[4] J. A. Bowden and R. Colton, *Aust. J. Chem.*, 21, 2657 (1968).

[5] J. A. Bowden, Ph.D. Thesis, University of Melbourne, 1972. Molecular weight measurements, performed osmometrically in chloroform and in benzene on $[Mo(CO)_4Br_2]_2$ and $[W(CO)_4I_2]_2$, have confirmed the dimeric formulation with seven-coordinate Mo(II) and W(II).

[6] H. Behrens and R. Schwab, *Z. Naturforsch. B*, 19, 768 (1964).

[7] J. K. Ruff, *Inorg. Chem.*, 7, 1821 (1968).

[8] E. W. Abel, I. S. Butler, and I. G. Reid, *J. Chem. Soc.*, 2068 (1963).

Table I. Electrochemical Data[a] for $Cr(CO)_5X^-NEt_4^+$

Electrochemical technique	Wave	Parameter[b]	Anion		
			$Cr(CO)_5Cl^-$	$Cr(CO)_5Br^-$	$Cr(CO)_5I^-$
Cyclic	1	E_p(ox)	0.67 V	0.71 V	0.73 V
		E_p(red)	0.60 V	0.64 V	0.66 V
	2	E_p(ox)	1.13 V	1.26 V	1.24 V
		E_p(red)			
Ac[c] (Fundamental harmonic)	1	E_p (∿)	0.66 V	0.68 V	0.70 V
		Half-width	105 mV	98 mV	95 mV
	2	E_p (∿)	1.12 V	1.14 V	1.18 V
		Half-width	130 mV	100 mV	98 mV
Pulse[d]	1	$E_{1/2}$	0.66 V	0.67 V	0.69 V
		Slope[e]	60 mV	60 mV	60 mV
Ac[c] (Second harmonic)	1	$E_{(I(2\omega t) = 0)}$			0.68 V
		$E_{\text{peak-to-peak}}$			70 mV
	2	$E_{(I(2\omega t) = 0)}$			1.20 V
		$E_{\text{peak-to-peak}}$			75 mV

[a] All data recorded at 20°. [b] All potentials quoted are volt *vs.* Ag|AgCl. [c] Alternating potential 10 mV p-p at 100 Hz. [d] Data for waves (2) not reported (distorted by maxima). [e] Slope of plot E *vs.* log $((i_l - i)/i)$.

Results and Discussion

I. Voltammetry at Pt Electrodes. A. $[Cr(CO)_5X]^-$.

At 20°, the chromium complexes gave two well-defined oxidation waves in acetone. Figure 1 shows a cyclic voltammogram of the iodo complex and Figure 2 an ac voltammogram. Under conditions of linear sweep voltammetry, the first (less positive) wave gave a constant value of $i_p/v^{1/2}$, where i_p is the peak current and v is the scan rate of dc potential. Furthermore, the value of the peak potential, E_p, was independent of scan rate. Under conditions of cyclic voltammetry, the separation of the peak potentials of the anodic and cathodic branches was 65 ± 5 mV. The separation in peak potential was found to be slightly less for iodide than bromide than chloride indicating a substituent effect on the charge-transfer rate constant. The separation in peak potentials was also found to be critically dependent upon the treatment and history of the Pt electrode. Using a platinum electrode freshly cleaned with a fine cloth, the data in Table I were obtained, and the first wave could be assigned to a reversible one-electron oxidation step. However, when the electrode was used for lengthy periods and scanned to more positive potentials than the second wave, the separation in E_p became substantially greater than 70 mV. However, the i_p values for both the anodic and cathodic branches of the cyclic voltammogram were close to unity under all conditions, and it would appear that, while always chemically reversible, the heterogeneous rate constant for the charge-transfer step is critically dependent on the nature of the Pt electrode surface. Fundamental harmonic ac voltammograms for the first wave were independent of scan rate with respect to both peak potential and peak height further confirming the reversibility of this electrode process. Thus, the peak potentials of the ac voltammograms were taken to be a measure of the reversible half-wave potential $E_{1/2}^r$ and they are listed in Table I. Second harmonic ac and pulse voltammograms were also indicative of reversible charge transfer, and it is concluded that the first oxidation process is a simple one-electron step

$$[Cr(CO)_5X]^- \rightleftharpoons Cr(CO)_5X + e^- \qquad (1)$$

to produce the chromium(I) halopentacarbonyl complex. In the case of the iodo species, this complex has been isolated,[1] and controlled potential electrolysis at +1.0 V gave a solution of the expected blue-green color. However, only limited stability was observed for this species at room temperature, and decomposition was indicated by a change in color 5 min after completion of the electrolysis. This observation is also consistent with the known chemical properties[1] of $Cr(CO)_5I$.

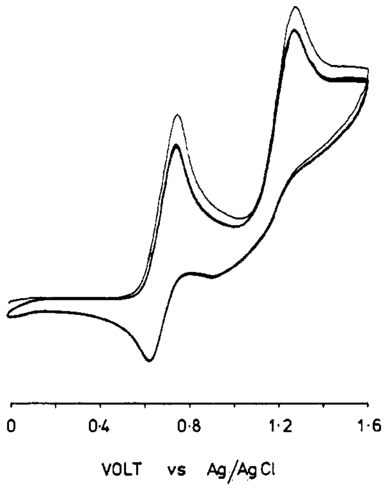


Figure 1. Cyclic voltammogram of $Et_4N[Cr(CO)_5I]$ at a platinum electrode: $T = 20°$; scan rate = 200 mV/sec.

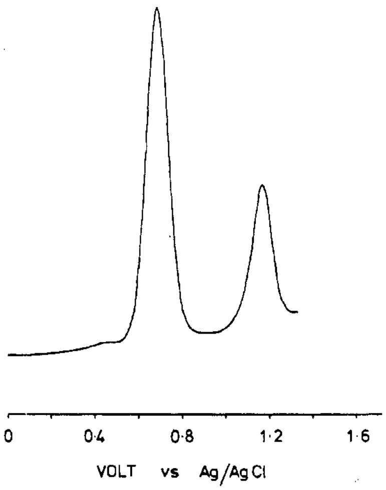


Figure 2. Linear sweep ac voltammogram of $Et_4N[Cr(CO)_5I]$ at a platinum electrode: $T = 20°$; scan rate = 100 mV/sec; alternating potential = 10 mV (p-p); frequency = 100 Hz.

Prior to this work only the chromium(I) iodo species had been isolated. Electrochemical data given in Table I show that the E° values for all the $[Cr(CO)_5X]^-/Cr(CO)_5X$ couples are very similar, and it should be possible to isolate the bromo and chloro analogs under suitably controlled conditions. The syntheses of these new chromium(I) halocarbonyls are currently under detailed investigation.[9] Preliminary infrared evidence has indicated the formation of $Cr(CO)_5Br$ (by analogy with the published spectrum[10] of $Cr(CO)_5I$). It is expected that at a later date a complete characterization of these compounds will be communicated.

The cyclic voltammograms of the second (more positive) electrode process (Figure 1) show considerably more complexity and a simple reversible step is not observed. The ac voltammogram shown in Figure 2 reveals that while the height of the second wave is less then the reversible one-electron step exhibited in the first wave, the electron-transfer step must still be rapid. Figure 3 shows a pulse voltammogram of both waves, which are of approximately equal height. This and the ac data define both waves as one-electron oxidation steps. Detailed analysis of the cyclic, ac, and pulse data reveals that the second wave exhibits reversible charge transfer with a follow-up chemical reaction. Equation 2 represents the electrode process.

$$Cr(CO)_5X \overset{e^-}{\rightleftharpoons} [Cr(CO)_5X]^+ \xrightarrow{k} \text{decomposition products} \quad (2)$$

In view of the presence of an assumed follow-up chemical reaction and its possible temperature dependence, the low-temperature electrochemistry of the $[Cr(CO)_5X]^-$ systems was undertaken in the hope that the $[Cr(CO)_5X]^+$ species would be stable at such temperatures. At 0°, all three complexes showed similar behavior to that at 20°. At −75°, however, two chemically reversible one-electron oxidation steps were observed. Figure 4 shows a cyclic voltammogram of the iodo complex at −75° and Figure 5 an ac voltammogram at the same temperature. The reversibility at this temperature is clearly seen now under both cyclic and ac conditions, and the follow-up chemical reaction has been quenched. All three complexes gave essentially identical behavior. Thus, the $[Cr(CO)_5X]^+$ species are found to be completely stable on the electrochemical time scale at −75°, and for the first time evidence for the existence of a chromium(II) halocarbonyl is reported. The electrochemistry at low temperatures is fully explained by eq 3.

$$[Cr(CO)_5X]^- \overset{e^-}{\rightleftharpoons} Cr(CO)_5X \overset{e^-}{\rightleftharpoons} [Cr(CO)_5X]^+ \quad (3)$$

Previously reported synthetic work[1-3] on the oxidation of $[Cr(CO)_5I]^-$ is entirely consistent with the electrochemical oxidation steps. Each of peroxide, Fe(III), and I_2 leads to the formation of $Cr(CO)_5I$. However, as Table I shows, there is a considerable separation in potentials required for further oxidation to the chromium(II) state, and previously used chemical oxidants would not be sufficiently powerful to produce a chromium(II) species. The absence in the literature of chromium(II) carbonyl halides is therefore readily explained. Furthermore, if more powerful oxidants were used, unless the oxidations had been carried out at very low temperatures, $[Cr(CO)_5X]^+$ would not have been isolated in view of the inherent instability of the complex. This, coupled with the rather positive oxidation potentials required for its synthesis, suggest it will be extremely difficult to characterize the $[Cr(CO)_5X]^+$ complex.

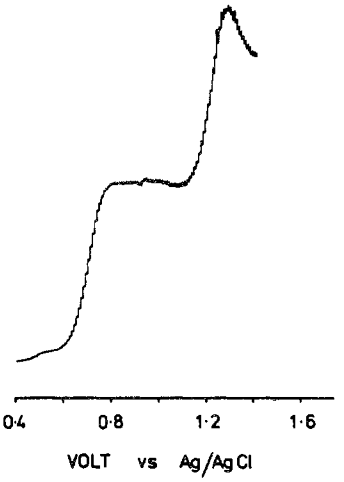


Figure 3. Pulse voltammogram of $Et_4N[Cr(CO)_5I]$ at a platinum electrode: $T = 20°$; scan rate = 10 mV/sec. Pulse applied at 1-sec intervals and current sampled for 15 msec.

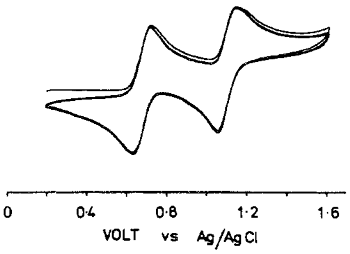


Figure 4. Cyclic voltammogram of $Et_4N[Cr(CO)_5I]$ at −75°. Other conditions are the same as in Figure 1.

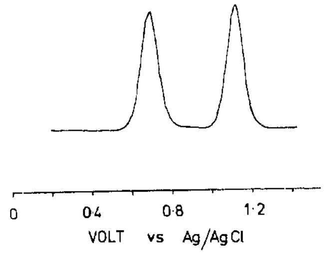


Figure 5. Linear sweep ac voltammogram of $Et_4N[Cr(CO)_5I]$ at −75°. Other conditions are the same as in Figure 2.

To verify that the solvent used was not playing a predominant role in the electrochemistry of the chromium pentacarbonyl complexes, measurements were repeated in dichloromethane. Essentially identical results were obtained, and the room temperature instability of $[Cr(CO)_5X]^+$ was confirmed.

Data obtained at glassy carbon electrodes were essentially identical with those found on Pt.

B. $[Mo(CO)_5X]^-$ and $[W(CO)_5X]^-$. Figure 6 shows cyclic voltammograms of the $[W(CO)_5I]^-$ and $[W(CO)_5Cl]^-$ species at a Pt electrode. All species characteristically gave a well-defined (less positive) oxidation wave and a broad, drawn out second wave. No reduction waves were observed at Pt electrodes on the reverse scan of the voltammograms. The Mo species were not completely stable in acetone, and some decomposition was observed after about 2 to 5 min. However, the electrochemistry was essentially identical with the stable tungsten species and, provided measurements on the Mo species are undertaken immediately on dissolution, results are considered to be reliable. Figure 7 shows an ac voltammogram of one of these complexes. Despite the fact that the cyclic voltammograms do not indicate reversibility, the ac scans of the first electrode process give

[9] A. M. Bond, J. A. Bowden, R. Colton, and Z. Sztajer, University of Melbourne, 1973.

[10] E. Lindner and H. Behrens, *Spectrochim. Acta*, 23, 3025 (1967).

Table II. Electrochemical Data[a] for $Mo(CO)_5X^-NEt_4^+$ and $W(CO)_5X^-NEt_4^+$

Electrochemical technique	Wave	Parameter[b]	Anion					
			$[Mo(CO)_5Cl]^-$	$[Mo(CO)_5Br]^-$	$[Mo(CO)_5I]^-$	$[W(CO)_5Cl]^-$	$[W(CO)_5Br]^-$	$[W(CO)_5I]^-$
Cyclic	1	E_p	0.83 V	0.85 V	0.88 V	0.90 V	0.83 V	0.83 V
	2	E_p	1.32 V	1.29 V	1.32 V	1.30 V	1.24 V	1.24 V
Ac[c] (Fundamental harmonic)	1	E_p (∿)	0.80 V	0.81 V	0.79 V	0.81 V	0.84 V	0.77 V
		Half-width	130 mV	120 mV	90 mV	140 mV	105 mV	95 mV
	2	E_p (∿)	1.20 V	1.20 V	1.19 V	1.19 V	1.20 V	1.13 V
		Half-width	200 mV	200 mV	160 mV	230 mV	150 mV	145 mV
Pulse[d]	1	$E_{1/2}$	0.77 V	0.79 V	0.80 V	0.78 V	0.81 V	0.77 V
		Slope[e]	58 mV	50 mV	45 mV	48 mV	40 mV	32 mV

[a–e] As in Table I.

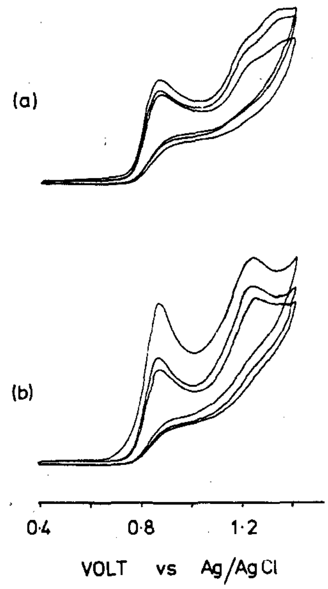


Figure 6. Cyclic voltammograms of (a) $Et_4N[W(CO)_5I]$ and (b) $Et_4N[W(CO)_5Cl]$ at a platinum electrode: $T = 20°$; scan rate = 200 mV/sec.

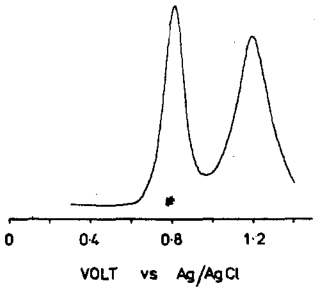


Figure 7. Linear sweep ac voltammogram of $Et_4N[W(CO)_5Cl]$ at a platinum electrode. Experimental conditions are the same as Figure 2.

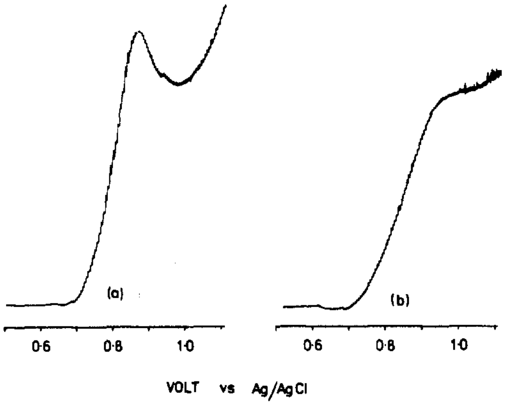


Figure 8. Influence of the platinum electrode surface on the shape of pulse voltammograms. Complex is $Et_4N[W(CO)_5Cl]$: (a) cleaned electrode; (b) used electrode. Experimental conditions are the same as in Figure 3.

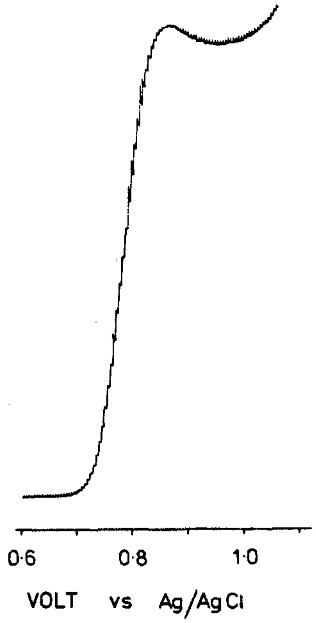


Figure 9. Pulse voltammogram of $Et_4N[W(CO)_5I]$. Experimental conditions are the same as in Figure 3.

sharp well-defined peaks. Table II summarizes some of the data. Figures 8a and 8b show the pulse polarograms of the first wave for $[W(CO)_5Cl]^-$ under conditions of an exhaustively cleaned Pt electrode and an electrode which had been used to record both waves. The slopes, although not the heights, are entirely different and, as was the case with chromium, the nature of the Pt electrode surface was extremely critical in defining the observed wave shapes. Under conditions of pulse polarography, plots of E *vs.* log $((i_l - i)/i)$, where E is the dc potential, i the current, and i_l the limiting current, were linear with slopes less than or equal to that expected for a reversible one-electron oxidation. Figure 9 shows a pulse polarogram of the first wave for the $[W(CO)_5I]^-$ complex. At a thoroughly cleaned Pt electrode the slope of an E *vs.* log $((i_l - i)/i)$ plot was 35 ± 5 mV and approached a value consistent with $n = 2$. However, in view of the cyclic voltammetric data, the electrode process cannot be defined as a simple reversible two-electron step.

The low-temperature electrochemistry on Pt of the Mo and W complexes failed to reveal any chemical reversibility in the cyclic voltammograms. Indeed at Pt electrodes, no evidence of reduction on the scan reversal step was observed under any conditions. Examination of the data in Tables I and II shows that the first oxidation for Mo and W in fact occurs at only slightly more positive potentials than the reversible Cr(0)–Cr(I)couple. Furthermore, the ac and pulse data are consistent with extremely rapid charge transfer. Consequently, the first stage of the electrode process can be adequately described as

$$[\mathrm{M(CO)_5X}]^- \overset{e^-}{\rightleftharpoons} \mathrm{M(CO)_5X} \qquad (4)$$

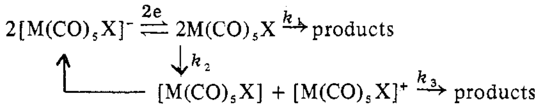
Obviously, the postulated Mo(I) species has no inherent stability at Pt electrodes.

Most follow-up chemical reactions or other irreversibility would lead to a considerable increase in ac half-width and slope of pulse E *vs.* log $((i_l - i)/i)$ plot compared with the simple reversible one-electron couple. The electrode process in question does not have these characteristics. However, the follow-up step is consistent with either a disproportionation or an ECE mechanism. Alternatively, the possibility of an adsorption blocking mechanism may also need to be considered.

In view of the chromium chemistry, the logical disproportionation mechanism to propose is

$$2\mathrm{M(CO)_5X} \xrightarrow{k} [\mathrm{M(CO)_5X}]^- + [\mathrm{M(CO)_5X}]^+ \qquad (5)$$

Despite the evidence[11] that in contrast with molybdenum(II) and tungsten(II), where seven coordination is favored, the most stable coordination number for chromium(II) is six, it has been shown in section IA that at room temperature $[\mathrm{Cr(CO)_5X}]^+$ has limited stability. It would be predicted, therefore, that the postulated molybdenum(II) and tungsten(II) analogs would be even more reactive. As a further complication, the $\mathrm{M(CO)_5X}$ species may also be reactive. However, the apparent n value of between 1 and 2 obtained in linear sweep, ac, and pulse experiments coupled with irreversible cyclics would be explained by the following mechanism for the first oxidation wave.



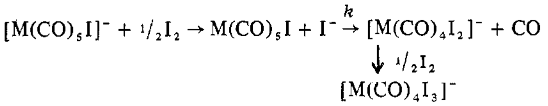
$$\begin{array}{l} 2[\mathrm{M(CO)_5X}]^- \overset{2e}{\rightleftharpoons} 2\mathrm{M(CO)_5X} \xrightarrow{k_1} \text{products} \\ \uparrow \qquad\qquad\qquad\quad \downarrow k_2 \\ \llcorner\!\!-\!\!-\!\!-\!\!- [\mathrm{M(CO)_5X}] + [\mathrm{M(CO)_5X}]^+ \xrightarrow{k_3} \text{products} \end{array} \qquad (6)$$

If k_3 were to be fast, then the apparent n value should approach 2, but of course chemically the system would be irreversible, as revealed by cyclic voltammetric data. The apparent value of n will lie between 1 and 2 depending on the values of k_1, k_2, and k_3. It can be noted that where X = Cl, the data actually gave a close fit to the mechanism without disproportionation, but for X = I an apparently multielectron step appears to be required. That the initial charge-transfer step is a reversible one-electron step seems to be completely substantiated by the data.

Alternatively, an ECE mechanism in which an initial electron-transfer step (E) is followed by a chemical reaction (C) and a further electron-transfer step (E) may be proposed. That is, a mechanism involving initial oxidation of $[\mathrm{M(CO)_5X}]^-$ to $\mathrm{M(CO)_5X}$, followed by a rearrangement or reaction to give another oxidation state (I) species which can itself be oxidized at less positive potentials than the $[\mathrm{M(CO)_5X}]^-$-$\mathrm{M(CO)_5X}$ couple, would be entirely consistent with the electrochemistry of the molybdenum and tungsten systems. For example eq 7 would be a suitable ECE mechanism.

$$[\mathrm{M^0(CO)_5X^-}] \overset{e^-}{\rightleftharpoons} \mathrm{M^I(CO)_5X} \xrightarrow{k_1} \mathrm{M^I}_x\mathrm{(CO)}_y\mathrm{X}_z \rightarrow \mathrm{M^{II}}_a\mathrm{(CO)}_b\mathrm{X}_c + e^- \qquad (7)$$

It is known[2,3] that when the $[\mathrm{Cr(CO)_5I^-}]$ species is oxidized by iodine the product is $\mathrm{Cr(CO)_5I}$. However, with Mo and W, the end product with the same oxidant is the seven-coordinate metal(II) anion $[\mathrm{M(CO)_4I_3}]^-$. The electrochemistry at Pt electrodes reveals that the first step for the Mo and W oxidation occurs at even more positive potentials than for Cr. Iodine, while capable of oxidizing $[\mathrm{M(CO)_5X}]^-$ species to $\mathrm{M(CO)_5X}$, is probably not a sufficiently powerful oxidant in its own right to produce the metal(II) product $[\mathrm{M(CO)_5X}]^+$ *via* an analogous two-step oxidation as found with chromium. However, the proposed disproportionation mechanism is entirely compatible with $[\mathrm{M(CO)_4I_3}]^-$ as the end product. The production of $[\mathrm{M(CO)_5I}]^+$ with iodine *via* a disproportionation mechanism leaves two iodide ions in solution which can substitute into the cation and produce the stable seven-coordinate species. Carbonyl compounds are readily substituted in this way.[8,12] Similarly, the ECE mechanism readily allows the production of a metal(II) species with iodine as an oxidant. An example of such a process might be



$$\begin{array}{l} [\mathrm{M(CO)_5I}]^- + {}^1\!/_2\mathrm{I_2} \rightarrow \mathrm{M(CO)_5I} + \mathrm{I}^- \xrightarrow{k} [\mathrm{M(CO)_4I_2}]^- + \mathrm{CO} \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow {}^1\!/_2\mathrm{I_2} \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad [\mathrm{M(CO)_4I_3}]^- \end{array} \qquad (8)$$

In view of the chemical reactions associated with the first oxidation wave for the Mo and W groups, it is not surprising that the second oxidation waves are extremely complex. Furthermore, they occur at rather positive potentials and have not been characterized. However, comparison of the height of this wave with the first wave suggests it is a multielectron step and probably results in the formation of high-oxidation state Mo and W species. In dichloromethane, the first oxidation wave has similar characteristics to that in acetone, but at more positive potentials additional complexities are observed. The abstraction of a halogen in such a solvent is always possible when reactive entities are being produced as in this study, and this may be occurring.

For the Mo and W complexes, voltammograms at glassy carbon electrodes were similar to those at Pt and provided no new information. However, polarography at mercury electrodes is substantially different from voltammetry at Pt or glassy carbon electrodes. Finally, although strong adsorption is indicated, and a self-inhibition or blocking mechanism could be consistent with the observed electrochemistry, this possibility is not considered in detail because of the similarity in E_p values for each of the complexes.

II. Polarography of $[\mathrm{M(CO)_5X}]^-$ Complexes at Dropping Mercury Electrodes (M = Cr, Mo, and W). The usable potential range at mercury electrodes is limited by the oxidation of mercury. Consequently, only the first oxidation wave for the complexes could be studied by polarography. Interestingly, on mercury electrodes, the first waves occurred at somewhat less positive potentials than on platinum, as Figure 10 shows for the $[\mathrm{Cr(CO)_5I}]^-$ complex.

At positive potentials relative to Ag-AgCl, the mercury electrode is positively charged. The electrocapillary maximum occurs at around 0 V *vs.* Ag-AgCl in acetone.[13] The complexes under consideration are negatively charged and contain halogen groups. Consequently, they and probably the products of oxidation are preferentially disposed toward adsorption at potentials where the oxidation occurs and adsorption severely influences the polarographic behavior par-

---

[11] J. Lewis, R. S. Nyholm, C. S. Pande, M. H. B. Stiddard, and S. S. Sandhu, *J. Chem. Soc.*, 3009 (1964).

[12] J. A. Bowden and R. Colton, *Aust. J. Chem.*, 22, 905 (1969).

[13] A. M. Bond, *J. Electrochem. Soc.*, 118, 1588 (1971).

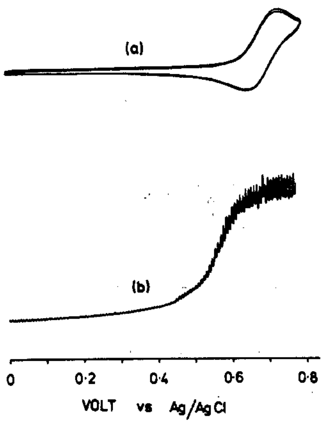


Figure 10. Difference in electrochemical behavior at platinum and mercury electrodes. Complex is $Et_4N[Cr(CO)_5I]$. (a) Cyclic voltammetry at platinum electrode. (b) Dc polarogram at dropping mercury electrode. Potential at which oxidation occurs at platinum is considerably more positive than at mercury.

ticularly with the iodo and bromo complexes. The chloro complexes are not so severely influenced by adsorption and are therefore more amenable to detailed study at mercury electrodes.

Figure 11 shows the first scan of a cyclic voltammogram of the $[Cr(CO)_5Cl]^-$ entity at a hanging drop mercury electrode. This and the polarographic data in Table III show that the system does not exhibit classically reversible electrochemistry at the mercury electrode. Indeed, subsequent to the first scan in the cyclic voltammetry, even broader waves than in Figure 11 are observed. The first scan, however, shows that chemically the system is reversible and the electrode process can be written as

$$[Cr(CO)_5Cl]^- \underset{ads}{\overset{ads}{\rightleftharpoons}} Cr(CO)_5Cl + e^- \qquad (9)$$

However, the $E_{1/2}$ value for this step is less positive than the value at Pt, and adsorption or even interaction with the mercury electrode is indicated. In the case of the $[Cr(CO)_5Br]^-$ and $[Cr(CO)_5I]^-$ complexes dc data show apparently greater reversibility, based on the slopes of the waves, and as was the case at Pt the heterogeneous charge-transfer rate constant is apparently fastest for the iodo complex.

With the Mo(0) and W(0) chloro complexes, some very interesting differences from the Pt electrode situation are revealed. Cyclic voltammograms of $[W(CO)_5Cl]^-$ at Pt and Hg electrodes are shown in Figure 12. A considerable degree of reversibility is indicated at mercury electrodes. This is in sharp contrast to results obtained at Pt and glassy carbon electrodes where no cathodic current is observed on the reverse scans. Thus, direct evidence for the existence of $W(CO)_5Cl$ and $Mo(CO)_5Cl$ has now been obtained. Figure 13 shows a dc polarogram for the $[W(CO)_5Cl]^-$ entity. The $E_{1/2}$ value, wave shape, and other polarographic characteristics of this chloro complex are almost identical with the $[Cr(CO)_5X]^-$ triad as shown in Table III. At mercury electrodes an almost reversible one-electron oxidation step is observed for the $[M(CO)_5Cl]^-$ species. However, as the cyclic voltammograms reveal for Mo and W, the $M(CO)_5Cl$ species still exhibit a certain degree of instability not found with the chromium group, and on the synthetic time scale their isolation is not expected. Apparently, the presence of mercury inhibits the follow-up reactions. The inhibition may arise from adsorption phenomena or even possibly direct interaction with mercury. For molybdenum and tungsten bromo and iodo species, adsorption is so severe that the electrode process is split into two main waves as

Table III. Polarographic Data[a] for $M(CO)_5X^-NEt_4^+$

Anion	$E_{1/2}$,[b] V	$n_{apparent}$[c]
$[Cr(CO)_5Cl]$	0.56	1.0
$[Cr(CO)_5Br]$	0.57	1.0
$[Cr(CO)_5I]$	0.58	1.0
$[Mo(CO)_5Cl]$	0.68	1.3
$[Mo(CO)_5Br]$	0.64, 0.75	1.5
$[Mo(CO)_5I]$	0.43, 0.79	1.5
$[W(CO)_5Cl]$	0.59	1.3
$[W(CO)_5Br]$	0.68, 0.80	1.9
$[W(CO)_5I]$	0.50, 0.77	2.0

[a] Recorded at 20° on 2.0×10^{-3} *M* solutions, with a controlled drop time of 0.16 sec. [b] All potentials quoted are volt *vs.* Ag|AgCl. [c] $n_{apparent}$ = (total limiting current for complex)/(total limiting current for chromium analog).

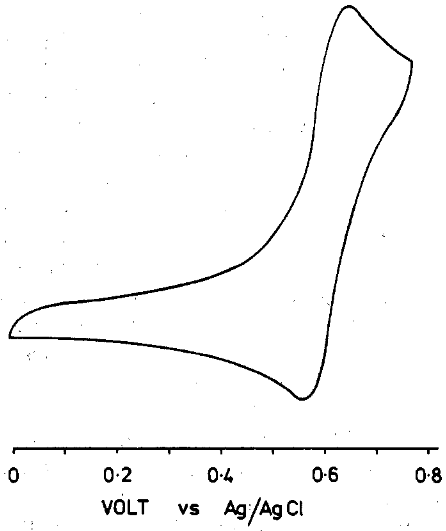


Figure 11. Cyclic voltammogram of $Et_4N[Cr(CO)_5Cl]$ at a hanging drop mercury electrode: $T = 20°$; scan rate = 200 mV/sec.

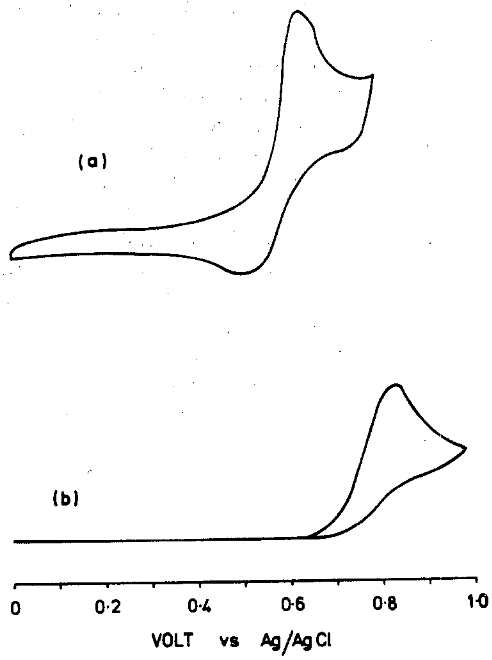


Figure 12. A comparison cyclic voltammogram at mercury and platinum electrodes. Complex is $Et_4N[W(CO)_5Cl]$: $T = 20°$; scan rate = 200 mV/sec. (a) Hanging drop mercury electrode; (b) platinum electrode.

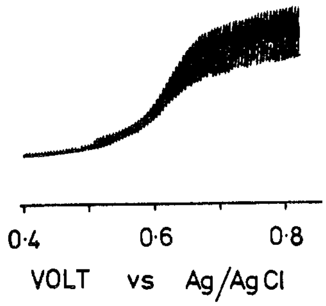


Figure 13. Dc polarogram of $Et_4N[W(CO)_5Cl]$ at 20°.

listed in Table III. The less positive wave is apparently a prewave corresponding to adsorption of reactant and/or product, and the second wave has an $E_{1/2}$ value close to those found at Pt. Figure 14 shows a polarogram of $[W(CO)_5I]^-$.

Assuming equal diffusion coefficients and measurement of limiting diffusion currents under controlled drop time conditions with a constant concentration of complex enables apparent n values to be calculated relative to the chromium system in which case n is known to be exactly one. The chloro complexes provide the best data because adsorption is minimized. Results of this experiment are tabulated in Table III. It is conceded that such calculations are not rigorous. However, it can be stated that the current per unit concentration values for all the chromium species are equal as required, despite the considerable variation in adsorption with change in halogen. For the Mo and W complexes, the apparent n values, based on this same type of calculation, lie between 1 and 2. The shapes of the polarographic waves are also consistent with apparent n values in this range. However, considerable adsorption apparent with the bromo and iodo complexes makes interpretation of results less certain than is the case with the chloro species. The substantiation of the $[W(CO)_5Cl]^-/W(CO)_5Cl$ couple by cyclic voltammetry at mercury electrodes and data for this and the molybdenum chloro complex are, however, excellent substantiation for the first part of the proposed mechanisms.

III. Relevance of Electrochemistry to Chemical Oxidation and Other Studies. Electrochemical data in this paper provide strong evidence for the existence of all three $Cr(CO)_5X$ species. Thus, six-coordinate chromium(I) halocarbonyls appear to have substantial stability. Further oxidation of the chromium(I) complexes leads to unstable six-coordinate $[Cr(CO)_5X]^+$ species. These are the first carbonyl halides of chromium(II) to be reported. Instability of this species is probably associated with its extreme reactivity (the $E°$ for the $Cr(CO)_5X$-$[Cr(CO)_5X]^+$ couple is very positive) and/or a possible preference for seven coordination.

The reason that chemical oxidation of $[Cr(CO)_5I]^-$ with iodine, ferric ions, or peroxide fails to produce a chromium(II) complex is now clear. They are simply not sufficiently powerful oxidants and are strong enough only to produce the reasonably stable $Cr(CO)_5I$ complex.

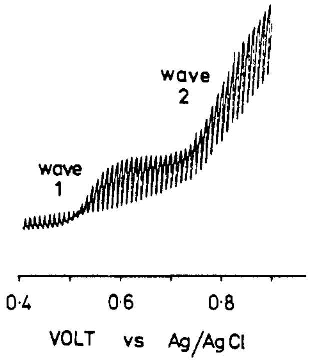


Figure 14. Dc polarogram of $Et_4N[W(CO)_5I]$: $T = 20°$.

The chemistry of the Mo and W halocarbonyl anions is indicated by the electrochemistry to be essentially similar to that of chromium except that, unlike chromium, the $M(CO)_5X$ (M = Mo and W) entities have no inherent stability and either disproportionate to the starting material and an M(II) complex or else rearrange or react to give another M(I) species which can be readily oxidized to a M(II) complex. In either case, it is not surprising that if chemical oxidation were to be carried out with bromine or iodine the end product isolated is $[M(CO)_4X_3]^-$. The above discussion and electrochemical findings are entirely consistent with the different oxidation products found on halogenation of $[Cr(CO)_5I]^-$ compared with the Mo and W analogs and provide a plausible explanation for this apparent discrepancy pointed out by King.[2]

An understanding of the probable mechanisms of oxidation of the $[M(CO)_5X]^-$ species obviously has important synthetic implications, and work in this area is to be followed up at a later date.

Furthermore, the marked difference between Pt and Hg electrodes, adsorption, and other phenomena imply that extremely interesting ligand-bridged electron transfers are probably involved in the oxidation processes. Fundamental electrochemical studies, using such techniques as potential-step chronocoulometry, etc., could therefore be considered for further study of the detailed nature of the charge-transfer steps.

Registry No. $Et_4N^+Cr(CO)_5Cl^-$, 14780-95-1; $Et_4N^+Cr(CO)_5Br^-$, 14780-93-9; $Et_4N^+Cr(CO)_5I^-$, 14780-98-4; $Et_4N^+Mo(CO)_5Cl^-$, 14780-96-2; $Et_4N^+Mo(CO)_5Br^-$, 15003-38-0; $Et_4N^+Mo(CO)_5I^-$, 14781-00-1; $Et_4N^+W(CO)_5Cl^-$, 14780-97-3; $Et_4N^+W(CO)_5Br^-$, 14780-94-0; $Et_4N^+W(CO)_5I^-$, 14781-01-2; $Cr(CO)_5Cl$, 15226-15-0; $Cr(CO)_5Br$, 14911-60-5; $Cr(CO)_5I$, 14911-59-2; $Cr(CO)_5I^+$, 43211-90-1; $Mo(CO)_5Cl$, 49569-23-5; $W(CO)_5Cl$, 14911-61-6.