Electrochemical Oxidation and Reduction of Binary Metal Carbonyls in Aprotic Solvents

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The electron-transfer reactions of several binary metal carbonyls at a Pt electrode in aprotic solvents have been investigated. In tetrahydrofuran, cathodic reduction of the carbonyls $M(CO)_n$ leads to the anions $[M_2(CO)_{2n-2}]^{2-}$ (M = Cr, Mo, W, and Fe) and $[M(CO)_n]^-$ (M = V), while reduction of the binuclear carbonyls $M_2(CO)_{10}$ (M = Mn and Re) gives the anions $[M(CO)_5]^-$. Of the anodic reactions, of particular interest are the oxidations of $Cr(CO)_6$ and $M_2(CO)_{10}$ (M = Mn and Re) which, in acetonitrile, produce the cations $[Cr(CO)_6]^+$ and $[M(CO)_5(NCMe)]^+$ respectively. The mechanisms of these electrode reactions have been studied.

ELECTROCHEMISTRY has an important role to play in the oxidation and reduction of organometallic compounds. For synthesis, the electrode has the advantages over chemical redox reagents that (*i*) by controlling the electrode potential it is possible to introduce energy selectively and hence, in many cases, to control or vary the number of electrons transferred, and (*ii*) the electrode is often able simply to add or remove an electron from the organometallic molecule whereas most redox reagents give more complex chemistry due to their ability to form bonds with the transition metal and to act as a nucleophile or an electrophile. In addition, electrochemical techniques are capable of giving much information about the ease of electron transfer and the intermediates in the redox processes and their chemical reactions.

In this paper we report an investigation of the oxidation and reduction of several metal carbonyls at a Pt electrode in aprotic solvents. The primary objectives were to identify the final products of these electrode reactions and to define the intermediates which might be useful for synthetic organic reactions and, indeed, it will be shown that several carbonyl cations and anions may readily be prepared and some of these are difficult to synthesise chemically. There have been some earlier limited investigations of the cathodic reduction of metal carbonyls;[1-3] these studies were all carried out at mercury electrodes, an electrode material which must be regarded as atypical because of the possibility for the formation of metal–mercury bonds. The only report of the successful anodic oxidation of simple metal carbonyls is a communication by the present authors.[4]

RESULTS

The electrochemistry of a wide range of metal carbonyls has been studied at a Pt electrode in the aprotic solvents tetrahydrofuran (thf), MeCN, CH_2Cl_2, and *NN*-dimethylformamide (dmf), containing tetrabutylammonium tetrafluoroborate (0·2M).† The potentials for the primary oxidation and reduction processes are summarised in Table 1. The results of a more detailed investigation are presented below.

TABLE 1

Primary oxidation and reduction potentials (in volts) for metal carbonyls at a Pt electrode. Peak potentials from cyclic voltammograms at 0·3 V s^{-1} are quoted *versus* the aqueous s.c.e. [Substrate] = *ca.* 5 × 10^{-3}M

	$-E_p^{red}$ in thf–$[Bu_4N][BF_4]$	E_p^{ox} in MeCN–$[Bu_4N][BF_4]$
$V(CO)_6$	0·21	No oxidation
$[Mn(CO)_5]^-$	No reduction	0·04
$Mn_2(CO)_{10}$	1·65	1·55
$Re_2(CO)_{10}$	2·36	1·55
$Cr(CO)_6$	2·66	1·53
$Mo(CO)_6$	2·59	1·53
$[Mo_2(CO)_{10}]^{2-}$	No reduction	No oxidation in thf
$[Mo_2H(CO)_{10}]^-$	2·91	No oxidation in thf
$W(CO)_6$	2·63	1·53
$[W_2(CO)_{10}]^{2-}$	No reduction	No oxidation in thf
$Fe(CO)_5$	2·38	1·51
$Ni(CO)_4$	2·70	1·26
CO	No reduction	No oxidation
$Fe(cp)_2$–$[Fe(cp)_2]^+$	−0·47	+0·44

cp = η-Cyclopentadienyl.

Reductions.—Group 6B *metal carbonyls.* Figure 1 shows a cyclic voltammogram for molybdenum hexacarbonyl in thf–0·2M-$[Bu_4N][BF_4]$. The important features are the reduction peak at E_p −2·59 V and the associated peak at E_p −2·14 V for the reoxidation of an intermediate produced in the primary reduction process. Experiments at low temperatures and very fast potential scan rates did not induce any reversibility in the reduction process. Under

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† 1M = 1 mol dm^{-3}.

[1] R. E. Dessy, F. E. Stary, R. B. King, and M. Waldrop, *J. Amer. Chem. Soc.*, 1966, **88**, 471.

[2] L. I. Denisovich, A. A. Ioganson, S. P. Gubin, N. E. Kolobova, and N. K. Anisimov, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1969, **2**, 218.

[3] P. Lemoine, A. Giraudeau, and M. Gross, *Proc. 25th I.S.E. Meeting*, Brighton, 1974, p. 458.

[4] C. J. Pickett and D. Pletcher, *J.C.S. Chem. Comm.*, 1974, 660.

the same conditions, chromium and tungsten carbonyls gave very similar cyclic voltammograms and data taken from cyclic voltammograms for all three metal carbonyls are presented in Table 2. It was found that peak currents for the reduction reactions, j_p^{red}, were proportional to the concentration of the metal carbonyls in the range 5×10^{-4}—5×10^{-2}M and also to the square root of the potential scan rate, v. Thus the reduction processes were diffusion controlled and this was confirmed by both rotating-disc and potential-step experiments. By comparison of the current function $j_p/v^{\frac{1}{2}}c$, with that for a known one-electron reaction, the reduction of fluorenone, it is also possible to conclude that the metal carbonyl reductions are also one-electron processes. The cyclic voltammograms recorded were unaffected by the addition of a proton donor, acetic acid, and by saturation of the solutions by carbon monoxide. The ratio of peak currents j_p^{anodic}/j_p^{red} was independent of the potential scan rate over the range 0·01—0·3 V s^{-1}. Thus it may be concluded that the intermediates reoxidised in the processes at $E_p \approx -2{\cdot}14$ V are stable, at least on the seconds time scale.

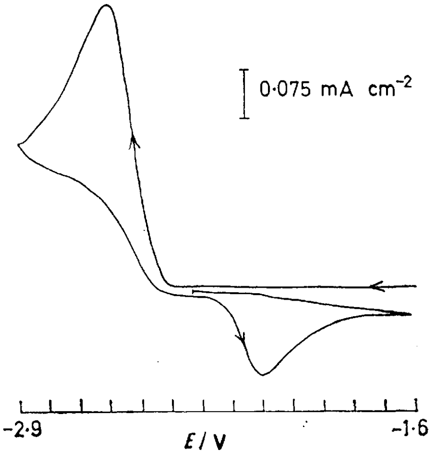

FIGURE 1 Cyclic voltammogram of $Mo(CO)_6$ (10^{-3}M) in thf–$[Bu_4N][BF_4]$ (0·2M) at a Pt electrode and a potential scan rate of 0·3 V s^{-1}

TABLE 2

Cyclic-voltammetric data for cathodic reactions of Group 6B metal carbonyls in thf–$[Bu_4N][BF_4]$ (0·2M) at a Pt electrode. Potentials *versus* the aqueous s.c.e. are quoted for a scan rate of 0·3 V s^{-1} and a concentration of 5×10^{-3}M. Range of potential scan rate 0·01—0·3 V s^{-1}. Note j_p^{anodic}/j_p^{red} is independent of v

	$-E_p^{red}$/V	$-E_p^{anodic}$/V	E_p^{red}/mV	$j_p^{red}/v^{\frac{1}{2}}c$ / µA mM^{-1} $V^{-\frac{1}{2}}$ $s^{\frac{1}{2}}$	j_p^{anodic}/j_p^{red}
$Cr(CO)_6$	2·66	2·10	−120	0·119	0·34
$Mo(CO)_6$	2·59	2·14	−90	0·124	0·32
$W(CO)_6$	2·63	2·13	−105	0·103	0·33
$[Mo_2H(CO)_{10}]^-$	2·91	2·14	−90		0·25
Fluorenone	2·06	2·00	−60	0·103	

Controlled-potential coulometry was carried out on solutions of each of the three metal carbonyls at potentials on, and more cathodic than, the reduction peaks. In all experiments it was confirmed that a single electron per molecule of carbonyl was transferred (see Table 3). During these electrolyses the disappearance of metal carbonyl was monitored by absorption spectroscopy in the u.v. region[5] and the linear plots of $[M(CO)_6]$ against q again infer the simple nature of the cathodic processes; the intercept on the q axis again gave $n = 1$. Figure 2 shows a typical set of results for a controlled-potential electrolysis of molybdenum hexacarbonyl and the results for all three metal carbonyls are summarised in Table 3.

TABLE 3

Coulometry and preparative studies of Group 6B metal carbonyls in thf–$[Bu_4N][BF_4]$ (0·2M)

	Potential/V	n_1[a]	n_2[b]	I.r. peaks (cm^{-1})
$Cr(CO)_6$	−2·7	1·2		1 905s, 1 870vs
$Mo(CO)_6$	−2·4	0·9		
	−2·6	1·1	1·1	1 883vs, 1 820s, 1 770w
	−2·9	1·2		
$W(CO)_6$	−2·6	1·1	1·1	1 880vs, 1 865sh, 1 770m
	−2·9	1·1	1·0	
$[Mo_2H(CO)_{10}]^-$	−2·9	1·0		1 883vs, 1 820s, 1 770w

[a] Based on the current consumed and extrapolation of linear j against q plots (q = charge passed during electrolysis). [b] Determined by extrapolation of linear $[M(CO)_6]$ against q plots; $[M(CO)_6]$ was determined spectrophotometrically.

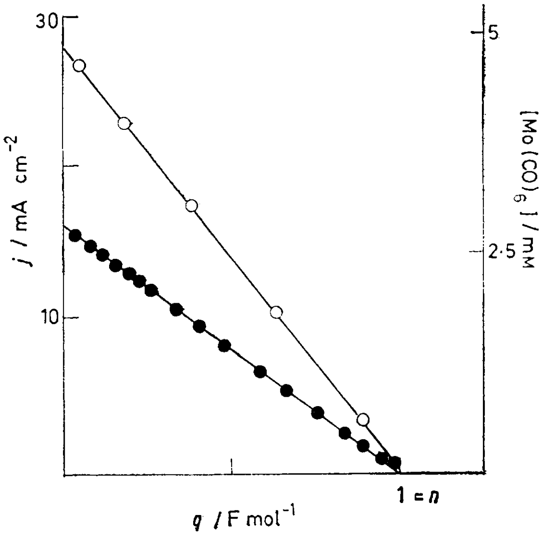

FIGURE 2 Controlled-potential coulometry for $Mo(CO)_6$ reduction in thf–$[Bu_4N][BF_4]$ (0·2M). Plots of j against q (●) and $[Mo(CO)_6]$ against q (○) at a potential of −2·6 V

After completion of the electrolyses, the catholytes were examined by i.r. spectroscopy. The spectrum obtained from the product of reduction of molybdenum hexacarbonyl is shown in Figure 3. Comparison of this spectrum with data in the literature[6-8] and with that of a chemically prepared sample showed that the electrolysis product is $[Mo_2(CO)_{10}]^{2-}$. Similar spectral[6-9] comparisons were made for the products from the reduction of chromium and tungsten hexacarbonyls (i.r. data are listed in Table 3) and hence it is clear that the overall electrode processes

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[5] T. L. Brown and D. J. Darensbourg, *Inorg. Chem.*, 1968, **7**, 959.

[6] R. G. Hayter, *J. Amer. Chem. Soc.*, 1966, **88**, 4376.

[7] W. F. Edgell and N. Pauuwe, *Chem. Comm.*, 1969, 284.

[8] H. Behrens and W. Haag, *Chem. Ber.*, 1961, **94**, 320.

[9] W. C. Kaska, *J. Amer. Chem. Soc.*, 1968, **90**, 6340.

are as in (1). Cyclic voltammetry on the catholytes at the end of the electrolyses showed that the dianions are not electroactive within the potential limits of the solvent.

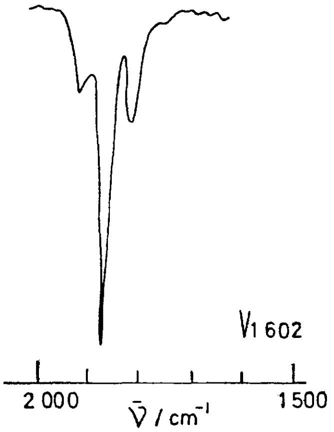

FIGURE 3 I.r. spectrum of catholyte at the end of the electrolysis of $Mo(CO)_6$ in thf–$[Bu_4N][BF_4]$ at a potential of $-2{\cdot}6$ V

Therefore the final products are not the origin of the anodic peaks observed on a cyclic voltammogram. A computer simulation showed that the ratios of peak currents j_p^{anodic}/j_p^{red} is close to that expected if the

$$M(CO)_6 + e^- \longrightarrow \tfrac{1}{2}[M_2(CO)_{10}]^{2-} + CO \ (M = Mo, Cr, \text{or } W) \quad (1)$$

electron-transfer processes (2) are slow and the anodic

$$M(CO)_6 + e^- \longrightarrow [M(CO)_6]^- \quad (2)$$

process is the reoxidation of the anion radical. (A low value for the rate constant, $k^{\ominus}$, for the heterogeneous electron-transfer reaction will cause the cathodic and anodic peaks to become separated, the separation and the peak current, j_p^{anodic}, depending on the value of $k^{\ominus}$.) An identical cyclic voltammogram would, however, arise if the initial electron transfer were followed by a rapid chemical reaction yielding a species electro-oxidisable at the potential of the anodic peak observed. Hence the quasi-stable intermediate in the reduction of these metal carbonyls cannot be positively identified. In view of the final products, however, they are likely to be one of the anion radicals $[M(CO)_6]^{\cdot -}$ or $[M(CO)_5]^{\cdot -}$. The anion

$$M(CO)_6 + e^- \longrightarrow [M(CO)_6]^{\cdot -} \xrightarrow{-CO} [M(CO)_5]^{\cdot -} \longrightarrow \tfrac{1}{2}[M_2(CO)_{10}]^{2-} \quad (3)$$

$[Mo_2H(CO)_{10}]^-$ was also studied by cyclic voltammetry and controlled-potential coulometry. It is reducible giving a diffusion-controlled peak ($j_p^{red} \propto v^{\frac{1}{2}}$) at E_p $-2{\cdot}91$ V and the preparative-scale electrolyses showed that $n = 1$ and the product is $[Mo_2(CO)_{10}]^{2-}$. The interesting feature of these experiments is that the cyclic voltammetry showed that the same intermediate is produced as in the reduction of molybdenum hexacarbonyl. This suggests that the electrode reaction leads to cleavage of the Mo–H–Mo bridge[10] and hence the quasi-stable intermediate in both reactions is $[Mo(CO)_5]^{\cdot -}$:

$$[Mo_2H(CO)_{10}]^- + e^- \longrightarrow \tfrac{1}{2}H_2 + 2[Mo(CO)_5]^{\cdot -} \longrightarrow [Mo_2(CO)_{10}]^{2-} \quad (4)$$

The electrochemistry of the Group 6B metal carbonyls was qualitatively the same when the solvent was MeCN or dmf. Indeed the potentials for the various processes show a marked similarity indicating that the solvent is never an important ligand.

Group 5B *metal carbonyls.* The cyclic voltammetry of $Mn_2(CO)_{10}$ at a Pt electrode in MeCN again showed a single reduction process although at a somewhat less cathodic potential, *i.e.* E_p $-1{\cdot}65$ V, and an associated anodic process at E_p $-0{\cdot}02$ V. The reduction process is diffusion controlled since $j_p^{red}/v^{\frac{1}{2}}$ was independent of v, and comparison of the current function $j_p^{red}/v^{\frac{1}{2}}c$ with that for fluorenone indicates the cathode reaction to be a two-electron process. The ratio j_p^{anodic}/j_p^{red} was $0{\cdot}55:1$ and was independent of potential scan rate. Controlled-potential coulometry carried out at potentials cathodic to the reduction peak confirmed that two electrons were transferred (see Figure 4). Furthermore the disappearance of $Mn_2(CO)_{10}$ during the electrolysis was followed using cyclic voltammetry and plots of $[Mn_2(CO)_{10}]$ against q were linear and extrapolated to the charge for a two-electron reaction.

At the end of the electrolyses, the catholytes were examined by i.r. spectroscopy and cyclic voltammetry.

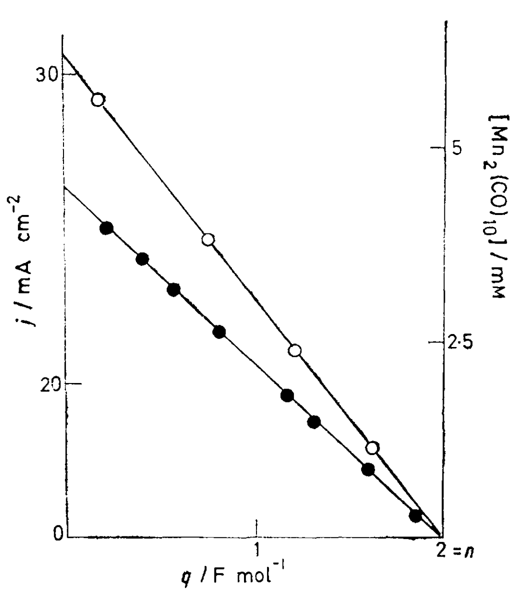

FIGURE 4 Controlled-potential coulometry for $Mn_2(CO)_{10}$ reduction in thf–$[Bu_4N][BF_4]$. Plots of j against q (●) and $[Mn_2(CO)_{10}]$ against q (○) at a potential of $-1{\cdot}7$ V

Figure 5 compares the cyclic voltammogram for this solution with one for a fresh solution of $Mn_2(CO)_{10}$; the curve after the electrolysis showed a primary oxidation process at E_p $-0{\cdot}02$V. Thus it is clear that the cyclic voltammetry produces no evidence for intermediates and that the anodic peak is for reoxidation of the stable final product. Comparison of the i.r. spectrum for the product solution (peaks at 1 863 and 1 898 cm^{-1}) with literature data[11] shows the product to be the anion $[Mn(CO)_5]^-$. Furthermore the product solution could be reoxidised anodically at $+0{\cdot}20$ V to reform $Mn_2(CO)_{10}$. Hence the reduction of the manganese carbonyl may be summarised as in (5).

$$Mn_2(CO)_{10} + 2e^- \underset{E_p\ -\ 0\cdot02V}{\overset{E_p\ -\ 1\cdot65V}{\rightleftharpoons}} 2[Mn(CO)_5]^- \quad (5)$$

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[10] E. W. Abel and F. G. A. Stone, *Quart. Rev.*, 1970, **24**, 498.

[11] W. Hieber and W. Schropp, *Chem. Ber.*, 1960, **93**, 455.

Cyclic voltammetry on $Re_2(CO)_{10}$ suggests its electrochemical behaviour to be as described for the manganese system. The rhenium carbonyl is, however, more difficult to reduce, the cathodic process occurring at E_p −2·36 V. The reverse anodic process takes place at E_p −0·1 V.

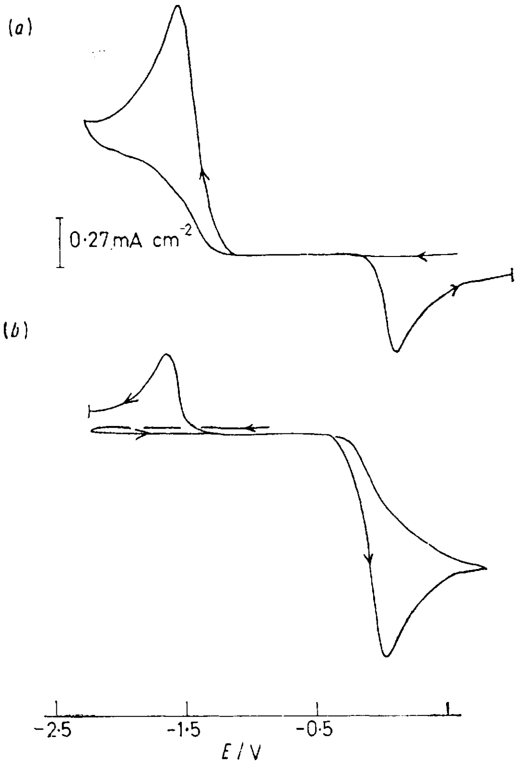

FIGURE 5 Cyclic voltammogram for solution of $Mn_2(CO)_{10}$ in thf–$[Bu_4N][BF_4]$ at a potential scan rate of 0·3 V s^{-1}: (a) before electrolysis; (b) after completion of a controlled-potential reduction

$$Re_2(CO)_{10} + 2e^- \underset{E_p\,-\,0{\cdot}1V}{\overset{E_p\,-\,2{\cdot}36V}{\rightleftharpoons}} 2[Re(CO)_5]^- \qquad (6)$$

Vanadium, iron, and nickel carbonyls. Cyclic voltammetry of the vanadium hexacarbonyl in MeCN showed that the couple $V(CO)_6$–$[V(CO)_6]^-$ is quasi-reversible. The reduction peak occurred at E_p −0·21 V and the peak separation ΔE_p = 270 mV. The peak shape factor $E_p^{red} - E_{p/2}^{red}$ = −135 mV. The cathodic and anodic peaks were the same height and in both cases $j_p/v^{\frac{1}{2}}$ was independent of v. On the other hand the curves for iron pentacarbonyl and nickel tetracarbonyl were similar to those for the molybdenum system. The reductions are diffusion controlled and there were associated anodic peaks for oxidation of quasi-stable intermediates. The cyclic voltammetric data are summarised in Table 4.

TABLE 4

Cyclic-voltammetric data in thf–$[Bu_4N][BF_4]$ (0·2M). Potentials *versus* the s.c.e. Other details as in Table 2

	$-E_p^{red}$ / V	$-E_p^{anodic}$ / V	$E_p^{red} - E_{p/2}^{red}$ / mV	j_p^{anodic}/j_p^{red} at 0·3 V s^{-1}
$Fe(CO)_5$	2·48	1·89	135	0·37
$Ni(CO)_4$	2·71	1·84	105	0·10

Controlled-potential coulometry shows the reduction of iron pentacarbonyl to be a one-electron process and i.r. spectroscopy on the catholyte at the end of the electrolysis showed the product to be the anion $[Fe_2(CO)_8]^{2-}$ (peaks at 1 920 and 1 850 cm^{-1}).[12] Hence the cathodic process is as in (7).

$$Fe(CO)_5 + e^- \longrightarrow CO + \tfrac{1}{2}[Fe_2(CO)_8]^{2-} \qquad (7)$$

Oxidations.—Group 6B *metals.* As has been reported in an earlier communication,[4] the anodic oxidation of chromium hexacarbonyl in MeCN–$[Bu_4N][BF_4]$ (0·2M) is of particular interest since there is clear evidence that the 17-electron cation $[Cr(CO)_6]^+$ is produced and is stable on the time scale of many seconds. Figure 6 shows cyclic voltammograms for the solution of chromium hexacarbonyl. The electrode process at E_p 1·53 V has all the properties of a reversible one-electron-transfer process; thus (*i*) ΔE_p = 60 mV, (*ii*) $E_p^{ox} - E_{p/2}^{ox}$ = 62 mV, (*iii*) the anodic and cathodic peak currents are equal for potential scan rates faster than 0·1 V s^{-1}, and (*iv*) at such scan rates and at room temperature the current function $j_p/v^{\frac{1}{2}}c$ is that for a one-electron process. At very slow scan rates there was evidence that the oxidation became more than a one-electron process and the ratio of cathodic to anodic peak current became less than one. Under such conditions it is certain that the overall electrode reaction is either an e.c.e. process or the initial electron transfer is followed by a disproportionation reaction. By lowering the solution temperature to −20 °C the rate of the chemical reaction was diminished to an extent that, even on the time scale of the slowest potential scan rates employed (0·01 V s^{-1}), the product of the single electron transfer was completely stable.

Under conditions where the anode reaction is a simple reversible one-electron process, the product must be the 17-electron cation $[Cr(CO)_6]^+$. This species should have an e.s.r. spectrum and, indeed, electrochemical oxidation of chromium hexacarbonyl at a potential on the first peak *in situ* in an e.s.r. cavity led to a spectrum with a single

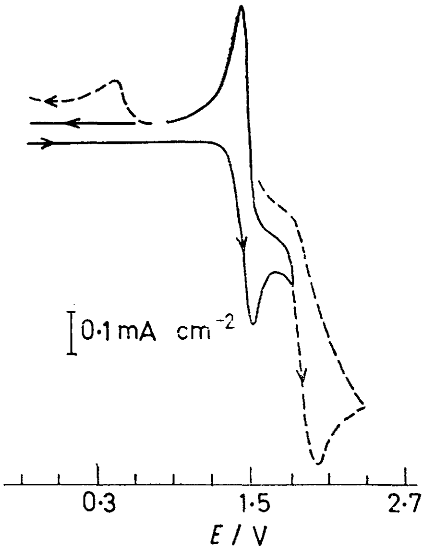

FIGURE 6 Cyclic voltammograms for the oxidation of $Cr(CO)_6$ (10^{-3}M) in MeCN–$[Bu_4N][BF_4]$ at a Pt electrode and a potential scan rate of 0·3 V s^{-1}

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[12] J. K. Ruff, *Inorg. Chem.*, 1968, **7**, 1818.

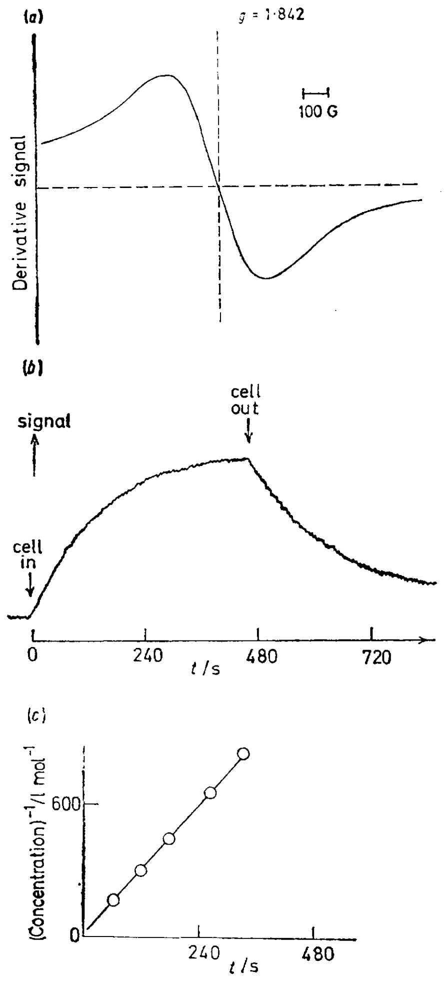


FIGURE 7 E.s.r. studies of the solution resulting from oxidation of $Cr(CO)_6$ (10^{-2}M) in MeCN–$[Bu_4N][BF_4]$: (*a*) e.s.r. spectrum of $[Cr(CO)_6]^+$; (*b*) growth and decay of e.s.r. signal during constant-current electrolysis (0·75 mA cm^{-2}) and after switching off the current when a steady-state signal was obtained; (*c*) kinetic plot for the second-order decay reaction of the cation produced

broad line, see Figure 7. The intensity of the signal grew with the duration of the electrolysis [Figure 7(*b*)] and, after interruption of the current, decayed by a second-order process, see Figure 7(*c*) ($k = 2{\cdot}5$ l mol^{-1} s^{-1} at 25 °C). This second-order process is probably disproportionation of the cation to give the unstable species $[Cr(CO)_6]^{2+}$.

Certainly on the longer time scale of a preparative electrolysis, coulometry at 1·60 V showed that the electrode reaction was an overall two-electron process and an i.r. spectrum of the anolyte at the end of the electrolysis did not show absorption peaks for CO-containing species. Hence the overall reaction probably has the mechanism in equations (8)—(10). The cyclic voltammogram for chromium hexacarbonyl showed a second oxidation peak at E_p 2·06 V for further oxidation of the cation $[Cr(CO)_6]^+$. A cathodic process at E_p 1·0 V is associated with this second irreversible oxidation and must be for reduction of one of

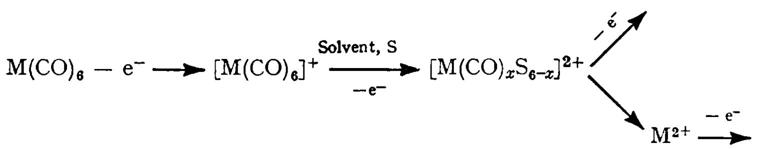
$$Cr(CO)_6 - e^- \longrightarrow [Cr(CO)_6]^+ \qquad (8)$$

$$2[Cr(CO)_6]^+ \xrightarrow{\text{slow}} Cr(CO)_6 + [Cr(CO)_6]^{2+} \qquad (9)$$

$$[Cr(CO)_6]^{2+} \xrightarrow{-\text{CO}} Cr^{2+} \qquad (10)$$

the intermediates in the decay of the dication; the relative peak current for this reduction process was dependent on the potential scan rate. Coulometry beyond the potential of the second peak showed that the process remains two electron and, again, i.r. spectra on the resulting anolyte solution showed no evidence for carbonyl species.

Cyclic voltammograms for solutions of tungsten and molybdenum hexacarbonyls showed no evidence for stable cationic carbonyls, and this is not surprising since these metals have a greater tendency than chromium to allow seven-co-ordination and hence any cation formed will be more prone to nucleophilic attack. The carbonyls gave voltammograms with a single major irreversible oxidation process at E_p 1·53 V and further less important and ill defined oxidation processes at more anodic potentials. In such cases there was a cathodic process for the reduction of an intermediate formed in the process at E_p 1·53 V; for molybdenum this peak was at E_p −0·32 V and for tungsten at E_p −0·44 V. The current functions for the process at E_p 1·53 V would suggest that the electrode processes are diffusion controlled and two-electron reactions on a short time scale and multielectron reactions on a longer time scale. Thus the probable oxidation mechanism is as in equation (11). Iron pentacarbonyl shows similar anodic behaviour.


(11)

$$M(CO)_6 - e^- \longrightarrow [M(CO)_6]^+ \xrightarrow[-e^-]{\text{Solvent, S}} [M(CO)_xS_{6-x}]^{2+} \begin{cases} \xrightarrow{-e^-} \\ \searrow M^{2+} \xrightarrow{-e^-} \end{cases} \qquad (11)$$

Group 5B *carbonyls*. In acetonitrile, $Mn_2(CO)_{10}$ gave a cyclic voltammogram with a single irreversible, but diffusion-controlled, anodic peak at E_p 1·56 V and an associated cathodic peak at E_p −1·32 V. The peak-current function indicates that the oxidation process involves the transfer of two electrons. This was confirmed by controlled-potential coulometry at + 1·65 V. Plots of *j* against *q* and $[Mn_2(CO)_{10}]$ against *q* were both linear and extrapolated to the charge for $n = 2$. The i.r. spectrum of the anolyte solution at the end of the electrolysis had peaks at 2 140w, 2 060s, and 2 045(sh) cm^{-1}, corresponding to the published spectrum [13] of the cation $[Mn(CO)_5(NCMe)]^+$. A cyclic voltammogram of the product solution showed that this cation reduces at E_p −1·32 V and a controlled-potential reduction showed that $[Mn(CO)_5]^-$ is formed in this process. The cyclic voltammetry of $Re_2(CO)_{10}$ in MeCN suggests this system to be identical. Cyclic-

$$Mn_2(CO)_{10} + 2MeCN - 2e^- \xrightarrow{E_p 1{\cdot}56\text{ V}} 2[Mn(CO)_5(NCMe)]^+$$

$$2[Mn(CO)_5(NCMe)_n]^+ \xrightarrow[+2e^-]{E_p -1{\cdot}32\text{ V}} [Mn(CO)_5]^- \qquad (12)$$

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[13] N. G. Connelly and L. F. Dahl, *Chem. Comm.*, 1970, 880.

voltammetric data for both carbonyls is summarised in Table 5.

TABLE 5

Cyclic-voltammetric data for oxidations in MeCN–$[Bu_4N][BF_4]$ (0·2M). Other details as in Table 2

	E_p^{ox} V	$E_p^{cathodic}$ V	$E_p^{ox} - E_{p/2}^{ox}$ mV	$j_p^{cathodic}/j_p^{ox}$
$Mn_2(CO)_{10}$	1·56	−1·32	62	0·42
$Re_2(CO)_{10}$	1·56	−1·12	62	0·23

In methylene chloride the $Mn_2(CO)_{10}$ system was qualitatively the same as in MeCN, see Figure 8. At very fast potential scan rates (>100 V s^{-1}), however, the oxidation process showed signs of reversibility, indicating that the cation $[Mn_2(CO)_{10}]^+$ has some slight stability. The reduction peak for the species $[Mn(CO)_5(CH_2Cl_2)]^+$ was smaller than the peak for the corresponding species in MeCN and this suggests that it is not completely stable. In addition this reduction peak in CH_2Cl_2 occurred at less cathodic potentials than in MeCN and these differences are to be expected since CH_2Cl_2 is a weaker complexing agent than MeCN. This explanation was tested by carrying out cyclic voltammetry in CH_2Cl_2 to which a small quantity of MeCN had been added, see Figure 8. It is clear that in this mixed solvent it is the nitrile complex which is formed in the anodic process. Other nitrile complexes (*e.g.* octyl cyanide) could also be formed by oxidation in CH_2Cl_2–octyl cyanide.

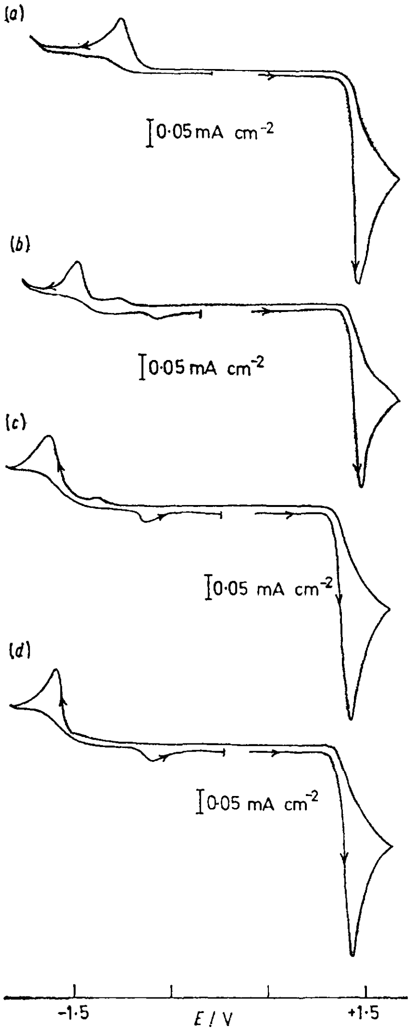

FIGURE 8 Cyclic voltammograms for $Mn_2(CO)_{10}$ oxidation at a Pt electrode in: (*a*) CH_2Cl_2–$[Bu_4N][BF_4]$ (0·2M); (*b*) CH_2Cl_2 + 10% MeCN–$[Bu_4N][BF_4]$ (0·2M); (*c*) CH_2Cl_2 + 10% n-$C_8H_{17}CN$–$[Bu_4N][BF_4]$ (0·2M); (*d*) MeCN–$[Bu_4N][BF_4]$ (0·2M)

DISCUSSION

Although the potentials listed in Table 1 are largely for irreversible electrode reactions and hence cannot be considered to be standard electrode potentials, it is interesting to note that the central metal atom has little effect on the oxidation and reduction potentials of uncharged binary metal carbonyls (excluding those with metal–metal bonds whose redox potentials are mainly dependent on the strength of this bond). In the case of the anodic oxidations, this similarity in the potentials arises because the electron is removed from a non-bonding orbital in the metal carbonyl while the reduction potentials are a reflection of the energies of the lowest unfilled antibonding orbitals; therefore it would appear that this energy level is not greatly dependent on the central metal [$V(CO)_6$ is an exception but is of course not isoelectronic with the other mononuclear carbonyls].

On the other hand, the charge on the carbonyl entity has a major effect on the redox potentials of an isoelectronic series. Table 6 shows some standard potentials estimated from cyclic voltammetry (all the reactions are reversible or nearly so). These indicate that there is a semiquantitative relation between the net charge and the redox potential; in the isoelectronic series $[V(CO)_6]^-$, $Cr(CO)_6$, and $[Mn(CO)_6]^+$ and $[Cr(CO)_5Br]^-$ and $[Mn(CO)_5Br]$ the effect of adding one positive charge is to make the oxidation more difficult by *ca.* 1·5 V. The replacement of CO by other ligands also has a marked effect on the standard potentials and it also seems possible to estimate the magnitude of the potential shift. For example in the isoelectronic pairs $Cr(CO)_6$–$[Mn(CO)_5Br]$ and $[V(CO)_6]^-$–$[Cr(CO)_5Br]^-$ the substitution of CO by Br makes oxidation more difficult by 0·7 V. Also a linear correlation between the reversible oxidation potentials for the series $[Mn(CO)_{6-n}(CNMe)_n]^+$ and *n* has been reported.[14] Hence it would seem possible by consideration of both charge and ligand-substitution effects to estimate the oxidation and reduction potentials for metal carbonyls in the 18-electron series containing a metal carbonyl of

TABLE 6

Standard electrode potentials (*versus* the s.c.e.) estimated from cyclic voltammetry

	$E^\ominus$/V
$V(CO)_6$–$[V(CO)_6]^-$	−0·05
$[Cr(CO)_6]^+$–$Cr(CO)_6$	+1·50
$[Mn(CO)_6]^+$–$Mn(CO)_6$	+3·00 [a]
$[Mn(CO)_5Br]^+$–$[Mn(CO)_5Br]$	+2·20
$[Cr(CO)_5Br]$–$[Cr(CO)_5Br]^-$	+0·70 [b]

[a] Estimated by extrapolation of data in ref. 14. [b] A. M. Bond, J. A. Bowden, and R. A. Colton, *Inorg. Chem.*, 1974, **13**, 84.

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known redox potential. Furthermore comparison of the potential shifts arising from substitution of CO by a set of ligands should allow the ligands to be placed in a series according to their relative net inductive effect on the remaining carbonyl fragment. Similar correlations have been reported for other types of complex.[15,16]

The final products identified from the cathodic reduction of the metal carbonyls in thf are those which might be expected since the same anions result from the chemical reduction with sodium amalgam or sodium metal in the same solvent at room temperature.[8,12,17,18] In the cases of the Group 6B metal and iron carbonyls, other products have been identified from the chemical reductions. For example in other solvents (*e.g.* liquid NH_3 [19] and $(Me_2N)_3PO$ [9]) a two-electron reduction of $Cr(CO)_6$ to $[Cr(CO)_5]^{2-}$ has been shown to occur and even in boiling thf treatment of $[Cr_2(CO)_{10}]^{2-}$ with caesium or potassium amalgam has been reported [9] to lead to $[Cr_2(CO)_9]^{4-}$. In all such reactions, however, it is possible to write mechanisms where the initial step is not electron transfer but ligand displacement or attack by nucleophiles or bases. Both the electroanalytical and preparative experiments carried out in the present study indicate that the anions $[M_2(CO)_{10}]^{2-}$ are not directly reducible.

The semi-stable intermediates formed in the cathodic reduction of the Group 6B metal carbonyls were tentatively proposed to be the anion radicals $[M(CO)_5]^{\cdot-}$. There is spectroscopic evidence for such intermediates in matrix-isolation experiments [20] and they have also been proposed as intermediates in the chemical reduction.[9] There is no previous evidence, however, that they might be stable for several seconds in solution; firm spectroscopic evidence for their presence in the electrolysis solution might be obtainable using suitable rapid-scanning i.r. equipment. The addition of species which might be expected to react with the carbonyl anions, *e.g.* alkyl bromides, certainly caused the anodic peak for the oxidation of the intermediate to disappear; hence, certainly, the intermediate or its precursor is a carbonyl anion.

The reduction of the binuclear carbonyls $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ led to the formation of $[Mn(CO)_5]^-$ and $[Re(CO)_5]^-$. Reoxidation of these products at Pt resulted in the isolation of the initial binuclear carbonyls. In earlier studies [1] using a mercury electrode such reoxidation experiments led to the organomercury compound $[Hg\{Mn(CO)_5\}_2]$. In most other respects the j–E curves found at Pt in this investigation are closely analogous to the behaviour using mercury as the electrode material.

The anodic oxidation of the binary metal carbonyls has not been reported by earlier authors. The chromium carbonyl cation has 17 electrons isoelectronic with vanadium hexacarbonyl and, although it has not been reported previously, it is not surprising to find it to be stable at least on the seconds time scale. The cation formed by the anodic oxidation of $Mn_2(CO)_{10}$ in acetonitrile, $[Mn(CO)_5(NCMe)]^+$, has been previously prepared by chemical oxidation with the nitrosyl cation; [13] it has been suggested that it is an ideal complex for the preparation of other manganese carbonyl complexes by ligand replacement. The cyclic voltammetric experiments in methylene chloride indicate that other nitrile complexes may be prepared electrochemically.

This investigation has shown conclusively that metal carbonyl anions and cations may readily be prepared electrochemically; indeed, some species difficult to prepare chemically may be synthesised by controlled-potential electrolysis. In addition, the electrochemical experiments show that there are often quasi-stable intermediates and these may be useful both for the synthesis of other organometallic molecules and in the construction of new organic reaction routes.

EXPERIMENTAL

Materials.—Tetrahydrofuran (Koch–Light) was purified by successive fractional distillations under a slow stream of nitrogen from KOH, CaH_2, and $Li[AlH_4]$. Acetonitrile (Koch–Light) was purified by the method of O'Donnell *et al.*; [21] *NN*-dimethylformamide (B.D.H.) was purified by distillation under reduced pressure from P_2O_5 and then anhydrous $CuCO_3$, and methylene chloride (B.D.H.) by fractional distillation from P_2O_5 and then anhydrous Na_2CO_3. All solvents were stored under nitrogen in the dark and in a dry-box. The supporting electrolyte $[Bu_4N][BF_4]$ was prepared by a standard procedure.[22] The binary metal carbonyls were obtained from Koch–Light or Alfa–Inorganics and were generally used without further purification. The salts $[Et_4N][Mo_2H(CO)_{10}]$ and $Na_2[Mo_2(CO)_{10}]$ were prepared according to literature procedures.[6,8]

Apparatus.—Electroanalytical experiments were carried out in a three-electrode cell. The working electrode was a smooth Pt wire, area 0·94 cm², and was surrounded by a Pt-spiral secondary electrode. The potential of the working electrode was probed by a Luggin capillary–reference electrode compartment whose position was made adjustable by mounting it on a syringe barrel. Coulometry and preparative experiments were carried out in a three-compartment H cell. The working electrode, a 1 cm² Pt gauze, was separated from the secondary electrode, a 2 cm² Pt gauze, by a grade 3 glass frit and from the reference electrode by an adjustable Luggin capillary and a tap. The working electrode compartment required 25 cm³ of solution which was stirred with a magnetic stirrer. The cell for the *in situ* e.s.r. spectroscopy consisted of a silica plate cell modified so that it contained a Pt-foil electrode in the cavity and a secondary lead electrode above the cavity; the radical was generated by a suitable constant-current electrolysis. In all solvents except acetonitrile,

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the experimental reference electrode was a Ag wire, but all potentials quoted in this paper have been adjusted to the aqueous standard calomel electrode (s.c.e.). In MeCN the reference electrode was a Radiometer aqueous s.c.e.

All electrochemical measurements were made with a Chemical Electronics valve potentiostat and waveform generator, type R.B. 2; *j–E* and *j–t* responses were recorded on a Hewlett-Packard Memory Scope type 1201A or a Bryans X-Y recorder, type 2600. The charges passed during electrolyses were measured using a Hi-Tek Instruments Current Integrator. E.s.r., u.v., and i.r. spectra were recorded on Varian E3, SP 800A, and SP 200G spectrometers respectively.

Procedures.—Cyclic voltammetry and pulse and rotating-disc experiments were carried out using solutions 0·2M in base electrolyte and concentrations of substrates in the range 10^{-4}—5×10^{-3}M. The experiments were carried out in a dry-box with a N_2 atmosphere and solutions were degassed with N_2 prior to the addition of the substrate. For most cyclic voltammetric experiments the range of potential scan rate was 0·01—0·3 V s^{-1}; in certain experiments the range was extended to 0·001—100 V s^{-1}. Controlled-potential electrolysis was also carried out under a nitrogen atmosphere and with thoroughly degassed solutions. An inlet with a silicone-rubber septum allowed samples to be taken with a syringe and these were diluted for examination by u.v., i.r. spectroscopy, *etc.* Typically the initial concentration of the substrate was 5×10^{-3}M.

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