Electrochemical Synthesis of Simple Metal Carbonyl Cations

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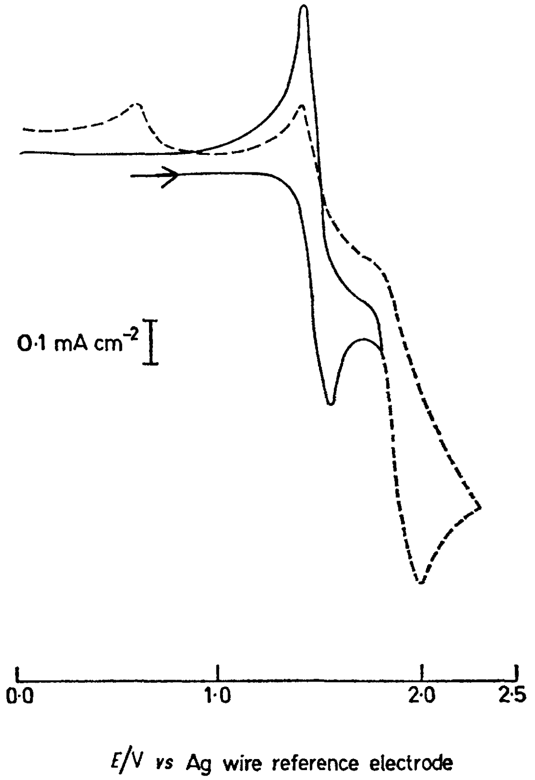
Summary It is shown that at a Pt electrode in MeCN–Bu_4NBF_4 (0·2M) chromium hexacarbonyl may be oxidised to the cation, $Cr(CO)_6^+$, a 17e species which has not previously been reported; the electrochemistry of other binary metal carbonyls is discussed briefly.

The Figure shows typical cyclic voltammograms for a solution of $Cr(CO)_6$ (5×10^{-3}M) in MeCN–Bu_4NBF_4 (0·2M) run at room temperature at a Pt electrode and at a potential scan rate of 0·3 V s^{-1}. Similar curves were obtained when the solvent was acetone or a gold electrode was used. The electrode reaction observed at + 1·44 V has all the properties of a simple reversible 1e transfer process (*i.e.*, $E_P^{OX} - E_P^{RED}$ 70 mV, $E_P^{OX} - E_{P/2}^{OX}$ 62 mV, i_P^{RED}/i_P^{OX} 1·0 and i_P^{OX} as for a known 1e oxidation) Hence the product of this anode reaction is the cation, $Cr(CO)_6^+$.



Cyclic voltammograms at slower potential scan rates show a dependence of i_P^{RED}/i_P^{OX} on the potential sweep rate from which it is possible to estimate that the cation has a half life of at least many seconds under the electrolysis conditions. At lower temperatures it was clear from cyclic voltammetry that the stability of the cation is greatly enhanced. A second irreversible 1e process is observed at more anodic potentials (Figure) and the electron transfer is accompanied by gas evolution.

The $Cr(CO)_6^+$ cation is a 17e species and hence should have an e.s.r. spectrum; electrochemical oxidation of the hexacarbonyl at a potential on the first wave *in situ* in an e.s.r. cavity led to a spectrum, with a single broad line. The intensity of the signal grew with the duration of the electrolysis and, after interruption of the current, decayed by a second-order process (*k ca.* 2·5 l mol⁻¹ s⁻¹), probably disproportionation of the cation. Certainly on the longer timescale of a controlled potential electrolysis the electrode process became an overall 2e reaction leading to the formation of a Cr^{II} species in solution.

$$Cr(CO)_6 - e \longrightarrow Cr(CO)_6^+$$

$$2Cr(CO)_6^+ \xrightarrow{\text{slow}} \underset{\text{unstable}}{Cr(CO)_6^{2+}} + Cr(CO)_6$$

Controlled potential coulometry at a potential on the plateau of the second wave showed the process remained an overall 2e reaction.

$$Cr(CO)_6 - 2e \longrightarrow \underset{\text{unstable}}{Cr(CO)_6^{2+}}$$

The cyclic voltammograms for solutions of $Mo(CO)_6$, $W(CO)_6$, and $Fe(CO)_5$ each showed a single irreversible 2e oxidation process. These may, however, be due to e.c.e. processes where the initial intermediate $M(CO)_n^+$ is highly unstable with respect to nucleophilic attack (*cf.* tendency for 7-co-ordination with Mo,W).[1] The cyclic voltammogram for a solution of $Mn_2(CO)_{10}$ also showed a single irreversible 2e oxidation process. In this case the product of controlled oxidation was identified as the cation $Mn(CO_5(MeCN)^+$ by i.r. spectroscopy [2140(w), 2060(s), 2045(sh) cm⁻¹].[2]

$$Mn_2(CO)_{10} - 2e \longrightarrow 2Mn(CO)_5^+ \xrightarrow{MeCN} 2(CO)_5Mn\text{–}N{=}C^+\text{–}Me$$

The chromium hexacarbonyl cation is novel in that it is isoelectronic with $V(CO)_6$, the only previously known **17e** binary carbonyl.[3] The electrochemical oxidation of binary carbonyls has not been hitherto investigated, yet it would seem that this technique could lead to the preparation of new carbonyl cations or intermediates for synthesis. Suitable redox reagents for the corresponding chemical synthesis are seldom available.

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