Anodic Oxidation of Metal Carbonyls in Trifluoroacetic Acid; Stabilities of some 17-Electron Cations

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The electrochemical oxidation of some metal carbonyls at a Pt electrode in trifluoroacetic acid–tetrabutylammonium tetrafluoroborate (0·2 mol dm^{-3}) is reported. It is shown that the 17-electron cations $[Cr(CO)_6]^+$, $[Fe(CO)_5]^+$, $[Mn(\eta\text{-}C_5H_5)(CO)_3]^+$, and $[MnBr(CO)_5]^+$ may be prepared from their parent 18-electron carbonyls and that each has some stability in this medium. The complex $[Mn_2(CO)_{10}]$ undergoes a two-electron oxidation and the product is $[Mn(CO)_5(O_2CCF_3)]$. This latter product can also be prepared by direct air oxidation.

IN a recent paper[1] we reported the electrochemical oxidation of binary metal carbonyls in aprotic solvents and, in particular, it was noted that the 17-electron cation $[Cr(CO)_6]^+$ was a metastable intermediate having a half-life of several seconds in acetonitrile. Trifluoroacetic acid (tfa) is a solvent of very low nucleophilicity and moderate acidity and it is known from studies of the oxidation of polynuclear hydrocarbons that cation radicals are much stabler species in this solvent than in aprotic solvents.[2,3] The object of the work in this paper was to investigate the electrochemical oxidation of metal carbonyls in tfa and to seek evidence for stable 17-electron cations.

EXPERIMENTAL

The instrumentation and most of the electrochemical cells have been described elsewhere.[1] The thin-layer cell for rapid coulometry was made from a 1-mm platinum-wire working electrode in a 1-mm precision-bore glass tube of length *ca.* 0.3 cm. To avoid end effects the end of the Pt wire had a glass bead. The reference electrode and secondary electrode were external to the thin layer. The volume of the thin layer (1.7×10^{-4} cm^3) was found from calibration experiments using a solution of ferrocene of known concentration.

Trifluoroacetic acid (tfa) was supplied by Fluorochem Ltd., $[Cr(CO)_6]$, $[Ni(CO)_4]$, and $[Mn_2(CO)_{10}]$ by B.D.H. Ltd., and $[Re_2(CO)_{10}]$, $[Mn(\eta\text{-}C_5H_5)(CO)_3]$, and $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2]$ by Alfa Inorganic Corporation. All were used without purification; the experimental data were unchanged following distillation of the tfa or sublimation of the $[Cr(CO)_6]$. $[NBu_4][BF_4]$ and $[MnBr(CO)_5]$ were prepared by literature methods.[1,4] All solutions used for electrochemical experiments were degassed with nitrogen.

E.s.r., u.v., and i.r. spectra were recorded on Varian E3, SP 800A, and SP 200G spectrometers respectively.

RESULTS

As a preliminary experiment, the stability of transition-metal carbonyls in tfa was checked by comparing the spectra of $[Cr(CO)_6]$ in this solvent with those in acetonitrile. The close similarity (Table 1) confirms the complete stability.

TABLE 1

Infrared and u.v. spectroscopic data for $[Cr(CO)_6]$ in the solutions used for the electrochemical studies; the spectra did not change with time

	I.r. ($\bar{\nu}$/cm^{-1})	U.v.	
		$\bar{\nu}$/cm^{-1}	ε/dm^3 mol^{-1} cm^{-1}
MeCN + 0.2 mol dm^{-3} $[NBu_4][BF_4]$	1 982vs	35 800	13 050
MeCN	1 980vs [a]	35 700 [b]	13 100
tfa + 0.2 mol dm^{-3} $[NBu_4][BF_4]$	1 985vs	35 842	12 980

[a] G. R. Dobson, M. F. Amr El Sayed, I. W. Stoltz, and R. K. Sheline, *Inorg. Chem.*, 1962, **1**, 576. [b] M. Wrighton, *Chem. Rev.*, 1974, **74**, 401.

Cyclic voltammograms were run over a wide range of potential scan rates for each of a series of metal carbonyls. The data for experiments at a Pt electrode in CF_3CO_2H–$[Bu_4N][BF_4]$ (0.2 mol dm^{-3}) are summarised in Table 2.

The cyclic voltammograms for $[Cr(CO)_6]$ and $[Mn(\eta\text{-}C_5H_5)(CO)_3]$ showed two oxidation processes. The first has all the characteristics[5,6] of a reversible one-electron process even at the slowest potential scan rates. Hence it is clear that the processes are (1) and (2) and that the cations

$$[Cr(CO)_6] - e^- \rightleftharpoons [Cr(CO)_6]^+ \qquad (1)$$

$$[Mn(\eta\text{-}C_5H_5)(CO)_3] - e^- \rightleftharpoons [Mn(\eta\text{-}C_5H_5)(CO)_3]^+ \qquad (2)$$

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[1] C. J. Pickett and D. Pletcher, *J.C.S. Dalton*, 1975, 879.

[2] O. Hammerich, N. S. Moe, and V. D. Parker, *J.C.S. Chem. Comm.*, 1972, 156.

[3] O. Hammerich and V. D. Parker, *Electrochim. Acta*, 1973, **18**, 537.

[4] W. Heiber, R. Schuch, and H. Fuchs, *Z. anorg. Chem.*, 1941, **248**, 243.

[5] R. S. Nicholson and I. Shain, *Analyt. Chem.*, 1964, **36**, 706.

[6] 'Physical Methods of Chemistry, Part IIa, 'Electrochemical Methods,' eds. A. Weissberger and B. W. Rossiter, Interscience, 1971.

have considerable stability. Indeed it is apparent that $[Cr(CO)_6]^+$ is considerably more stable in tfa than in MeCN,[1] the half-lives of both cations in tfa being many seconds and certainly outside the range determinable by cyclic voltammetry. The cation $[Mn(\eta\text{-}C_5H_5)(CO)_3]^+$ is bluish red and $[Cr(CO)_6]^+$ is colourless. The second oxidation processes at more positive potentials were totally irreversible. The magnitude of the peak currents at all potential scan rates suggests that this process is the formation of a highly unstable dication.

TABLE 2

Electrochemical data for the oxidation reactions of metal carbonyls in trifluoroacetic acid–tetrabutylammonium tetrafluoroborate (0.2 mol dm^{-3}) at a Pt electrode

	First oxidation process					Second oxidation
Complex	E_p^{ox} / V	$E_p^{ox} - E_{p/2}^{ox}$ / mV	$j_p^{ox}/v^{\frac{1}{2}}c$ / A cm^{-2}V$^{-\frac{1}{2}}$ s$^{\frac{1}{2}}$ dm^3 mol^{-1}	$E_p^{ox} - E_p^{red}$ / mV	j_p^{red}/j_p^{ox}	E_p^{ox} / V
$[Cr(CO)_6]$	1.09[a]	57	1.61	59	1.00[b]	1.69
$[Fe(CO)_5]$	0.65	57	1.65	57	0.58	None
$[Ni(CO)_4]$	0.80	61		*c*	*c*	None
$[MnBr(CO)_5]$	1.51	55	1.55	57	0.70	1.77
$[FeBr_2(CO)_4]$	1.86	59		*c*	*c*	2.25
$[Mn(\eta\text{-}C_5H_5)(CO)_3]$	0.79	57	1.53	72	1.0	1.98
$[Mn_2(CO)_{10}]$	0.99	49	3.17	*c*	*c*	2.20
$[Re_2(CO)_{10}]$	1.06	79	3.02	*c*	*c*	2.28
$[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2]$	1.05	98	3.00	*c*	*c*	1.27

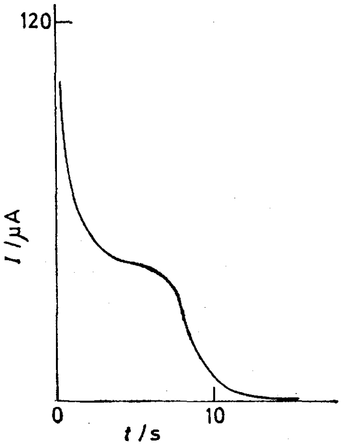
[a] Potentials *versus* the saturated calomel electrode. [b] Ratio measured with scan rate $v = 0.3$ V s^{-1}. [c] Irreversible.

The cyclic voltammograms of $[Fe(CO)_5]$ and $[MnBr(CO)_5]$ were similar to those for $[Cr(CO)_6]$ and $[Mn(\eta\text{-}C_5H_5)(CO)_3]$, except that those of $[Fe(CO)_5]$ showed only the first oxidation process and in both cases this first oxidation process only had the characteristics of a reversible one-electron process at faster potential scan rates. At slower scan rates the ratio j_p^{red}/j_p^{ox} became less than one, showing that the products of the electron-transfer reactions, $[Fe(CO)_5]^+$ and $[MnBr(CO)_5]^+$, have only limited stability in this medium at room temperature ($\tau_{\frac{1}{2}}$ 50—500 ms). The cyclic voltammograms for the other metal carbonyls showed only irreversible oxidation processes and there was no evidence for stable intermediates. In particular it should be noted that $[Ni(CO)_4]^+$ could not be detected even at the fastest potential scan rates. The current functions for the carbonyls with metal–metal bonds indicated that these species underwent two-electron oxidations.

The oxidations of $[Cr(CO)_6]$ and $[Mn(\eta\text{-}C_5H_5)(CO)_3]$ were investigated using thin-layer coulometry. The Figure shows a typical transient in the plot of I against time in response to a potential step experiment, 0.3 to 1.2 V; the areas under such curves were integrated and used to determine the number of electrons, n, transferred during the oxidation. The value of n for $[Cr(CO)_6]$ was 1.04 ± 0.04 (average of nine experiments) and for $[Mn(\eta\text{-}C_5H_5)(CO)_3]$ was 1.01 ± 0.05 (average of five experiments). Furthermore the stability of the products on the seconds timescale could be demonstrated by double-potential-step or cyclic-voltammetric experiments in the thin-layer cell. In each case the charge for the reverse process was identical to that for the oxidation.

E.s.r. spectra were also recorded for the 17-electron products. The cations were generated by constant-current electrolysis *in situ* in the e.s.r. cavity. The spectrum for $[Cr(CO)_6]^+$ showed a single very broad line ($\langle g \rangle$ 1.945) while that for $[Mn(\eta\text{-}C_5H_5)(CO)_3]^+$ was a six-line spectrum ($\langle g \rangle$ 2.015, $\langle a \rangle$ 92.5 G) * typical of radicals containing manganese. For each of the cations, their formation and decay during constant-current electrolysis and after interruption of the current were monitored at fixed field. Assuming that the concentration of radicals was uniform throughout the cavity, the kinetics of the loss of the cations could be estimated from the signal–time transient during the decay process. The reactions removing both cations were pseudo-first order and approximate half-lives were 60 s for $[Cr(CO)_6]^+$ and 10 s for $[Mn(\eta\text{-}C_5H_5)(CO)_3]^+$.

The anodic oxidation of $[Mn_2(CO)_{10}]$ was carried out in a conventional three-electrode cell using a solution in CF_3CO_2H–$[NBu_4][BF_4]$ (0.2 mol dm^{-3}) and a potential just positive to the first peak. The i.r. spectrum of the anolyte after the electrolysis included carbonyl peaks at 2 060 and 2 010 cm^{-1} and a cyclic voltammogram of the product solution showed an oxidation reaction at E_p 2.20 V, the potential of the second oxidation process of $[Mn_2(CO)_{10}]$. The coulometry confirmed the oxidation of $[Mn_2(CO)_{10}]$ as a two-electron process. It was also noted that in tfa $[Mn_2(CO)_{10}]$ underwent air oxidation. The reaction is rapid and a solution of $[Mn_2(CO)_{10}]$ in tfa reacted completely within 1 min when a stream of air was passed through the solution. The tfa was



Transient for the oxidation of $[Cr(CO)_6]$ in CF_3CO_2H + 0.2 mol dm^{-3} $[NBu_4][BF_4]$ in the thin-layer cell. Potential step, 0.3 to 1.2 V

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* 1 G = 10^{-4} T.

removed *in vacuo* and the i.r. spectrum of the remaining pale yellow solid showed peaks at 1 690, 2 010, and 2 060 cm^{-1}. The first peak was assigned to a carboxylate C=O stretch and the product was considered to be [Mn(CO)$_5$(O$_2$CCF$_3$)]. The product also gave a cyclic voltammogram with a single peak at E_p 2.20 V and hence it was concluded that the product of the electrochemical reaction was also [Mn(CO)$_5$-(O$_2$CCF$_3$)]. The direct air oxidation of [Mn$_2$(CO)$_{10}$] does not occur in aprotic solvents. The complex [{Fe(η-C$_5$H$_5$)-(CO)$_2$}$_2$] also reacted rapidly with air in tfa and hence it is suggested that air oxidation of metal–metal-bonded carbonyls may be a general reaction in this medium. The i.r. spectrum of the red-brown solid isolated from the second preparation had peaks at 2 060s, 2 020s, and 1 685m cm^{-1}, compatible with [Fe(η-C$_5$H$_5$)(CO)$_2$(O$_2$CCF$_3$)] (lit.:[7] 2 059s 2 019s, and 1 680m cm^{-1}).

DISCUSSION

As expected, tfa appears to be an excellent solvent for the electrochemical generation and study of metal carbonyl cations. It is clear that the 17-electron cations [Cr(CO)$_6$]$^+$, [Mn(η-C$_5$H$_5$)(CO)$_3$]$^+$, [Fe(CO)$_5$],$^+$ and [MnBr-(CO)$_5$]$^+$ may all be prepared by electrochemical oxidation of their parent 18-electron carbonyls in tfa, and that each of these species has some stability in this medium. Indeed the first two carbonyl cations have half-lives of several seconds even at room temperature and their stabilities could, of course, be increased by lowering the temperature.

The stability of the carbonyl cations in tfa reflects directly that in MeCN.[1] The half-lives of the binary carbonyl cations increase in the order Ni $<$ Fe $<$ Cr and since, in fact, the cations [Mo(CO)$_6$]$^+$ and [W(CO)$_6$]$^+$ could not be detected it would appear that the carbonyls with highly co-ordinated and small metal centres have the highest stability. The decay reactions of [Cr(CO)$_6$]$^+$ and [Mn(η-C$_5$H$_5$)(CO)$_3$]$^+$ have been shown to be pseudo-first order. Hence the likely decay route involves nucleophilic attack by the solvent or loss of a molecule of carbon monoxide. The chemical behaviour of these 17-electron carbonyl cations is, however, not yet well defined and will be the subject of further investigations; the 17-electron species [V(CO)$_6$] and the 18-electron cation [Mn(CO)$_6$]$^+$ may not be good models.

The carbonyls [Mn$_2$(CO)$_{10}$] and [{Fe(η-C$_5$H$_5$)(CO)$_2$}$_2$] undergo rapid air oxidation leading to cleavage of the metal–metal bond and formation of [Mn(CO)$_5$(O$_2$CCF$_3$)] and [Fe(η-C$_5$H$_5$)(CO)$_2$(O$_2$CCF$_3$)] respectively. These reactions do not occur in aprotic solvents and the mononuclear carbonyls are not oxidised by air. The oxidation by air of the iron species in aqueous perchloric acid has, however, been reported.[8] It would therefore appear that protons are essential for the binuclear carbonyls to react with air, but their rôle is not clear. The anodic reactions lead to the same products although this reaction route seems to have no advantages. Indeed, the air oxidation is more convenient. It may be noted that the anodic oxidation of [Mn$_2$(CO)$_{10}$] is essentially similar in acetonitrile;[1] the oxidation leads to cleavage of the metal–metal bond and formation of [Mn(CO)$_5$(NCMe)]$^+$.

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