

THE ELECTROCHEMICAL BEHAVIOR OF METAL CARBONYLS IN A
MIXTURE OF A ROOM TEMPERATURE MOLTEN SALT AND BENZENE

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ABSTRACT

The electrochemical oxidation of six metal carbonyls was studied in a mixture of the high Lewis acid, room temperature molten salt, composed of aluminum chloride and ethylpyridinium bromide (2:1 molar ratio) and benzene (50% v/v). Chromium hexacarbonyl was found to be reversibly oxidized to the seventeen electron cation $\text{Cr}(\text{CO})_6^+$, isoelectronic with vanadium hexacarbonyl. Some stability was also found for the corresponding 17 electron cation of iron pentacarbonyl. The other carbonyl compounds studied $\text{Mo}(\text{CO})_6$, $\text{W}(\text{CO})_6$, $\text{Re}_2(\text{CO})_{10}$, and $\text{Mn}_2(\text{CO})_{10}$ exhibit electrochemical behavior characteristic of chemical and electrochemical reactions following the electron transfer reaction. Based on the large dependence of the oxidation potentials on the nature of the central metal atom in this solvent, it is proposed that the metal carbonyls interact with electron deficient species in the melt, decreasing the σ donor ability of the ligand, but increasing its π acceptor capabilities.

INTRODUCTION

The electrochemical behavior of metal carbonyls in aprotic solvents was recently described by Pickett and Pletcher^{2,3}. Chromium hexacarbonyl was found to be reversibly oxidized to $\text{Cr}(\text{CO})_6^+$, thus demonstrating the exceptional stability of this 17 electron cation, isoelectronic with vanadium

hexacarbonyl. The other carbonyl compounds studied, e.g., $\text{Fe}(\text{CO})_5$, $\text{Mo}(\text{CO})_6$, $\text{W}(\text{CO})_6$, and the binuclear carbonyls $\text{Re}_2(\text{CO})_{10}$ and $\text{Mn}_2(\text{CO})_{10}$ were all found to exhibit chemical and electrochemical reactions following the electron transfer step.

The molten salt system composed of aluminum chloride and ethylpyridinium bromide⁴ in a 2:1 molar ratio is a high Lewis acidity medium, liquid at room temperature. Recently studies have shown that this medium can be used for electrochemical studies of organometallic and organic compounds⁵. An electrochemical window of -0.2 to 1.8 V vs. Al reference electrode allows the investigation of electrochemical oxidations. The molten salt is miscible with benzene and the 50% v/v mixture was shown to be suitable for the study and preparative electrooxidation of hexamethylbenzene⁶.

In the present paper the electrochemical oxidation of six metal carbonyls is described in the 50% v/v mixture of 2:1 aluminum chloride:ethylpyridinium bromide (=Et py Br) melt and benzene.

EXPERIMENTAL SECTION

All experiments were carried out at $28 \pm 3^\circ\text{C}$ under a prepurified nitrogen atmosphere in a Vacuum Atmospheres Co. drybox equipped with a model HE-493 Dri-Train.

A three-electrode electrochemical cell described earlier⁶ was used. A vitreous carbon working electrode, a disk of 2.7 mm of diameter (Atomergic Chemicals, V 10 or V 25 grade) sealed in pyrex⁷ was polished and buffed on a polishing wheel with a 0.1 micron alumina prior to use.

Cyclic voltammograms were recorded on a multipurpose instrument⁶ in conjunction with a Houston Instruments Omnigraph 2000 X-4 recorder. Normal pulse voltammograms were obtained using a PARC Model 174 Polarographic Analyzer.

All metal carbonyl compounds (Alfa-Strem or Research Organic (Inorganic) Chemicals) were used without further purification. Melt preparation and purification is described elsewhere⁶.

Due to the low solubility of the metal carbonyls in pure melt, solutions of these compounds were made up in benzene (Spectrograde, Fischer). After

complete dissolution of the carbonyl compound, an equal volume of melt was added to benzene solution.

RESULTS AND DISCUSSION

A normal pulse voltammogram of chromium hexacarbonyl in the 2:1 AlCl_3 : EtpyBr melt plus benzene (50% v/v) on a vitreous carbon working electrode is shown in Figure 1. Analysis of $\log i/i_d - i$ vs. E reveals a linear plot with a 55 ± 5 mV slope, indicative of a one-electron reversible oxidation process, with a $E_{1/2} = 1.52$ V vs. Al reference electrode.

Cyclic voltammograms for chromium hexacarbonyl as a function of scan rate are shown in Figure 2. The peak potentials are independent of scan rate (v). The ratio $i_{p_a}/v^{1/2}$ is independent of scan rate with 5%, thus indicating that the electrode process is diffusion controlled. The ratio i_{p_a}/i_{p_c} , calculated following Nicholson's procedure⁸, is unity in this range of scan rates ($0.1 - 0.5$ V sec^{-1}). The peak potential separation is 80 mV due largely to non-compensated IR drop.

These data indicate that chromium hexacarbonyl is electrochemically oxidized in this medium to the stable carbonyl cation $\text{Cr}(\text{CO})_6^+$. The oxida-

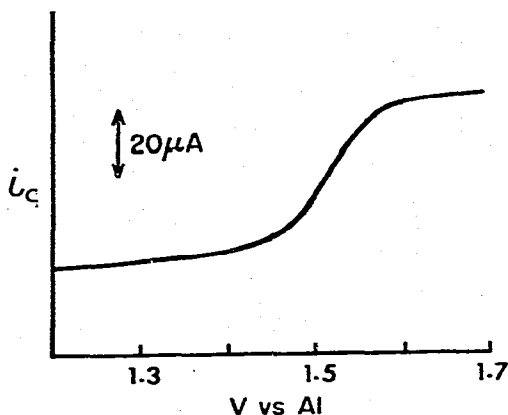


Figure 1 - Normal pulse voltammogram of 1×10^{-3} M solution of $\text{Cr}(\text{CO})_6$ in the mixture of the 2:1 aluminum chloride ethylpyridinium bromide melt and benzene (50% v/v) on a vitreous carbon working electrode at 28°C.

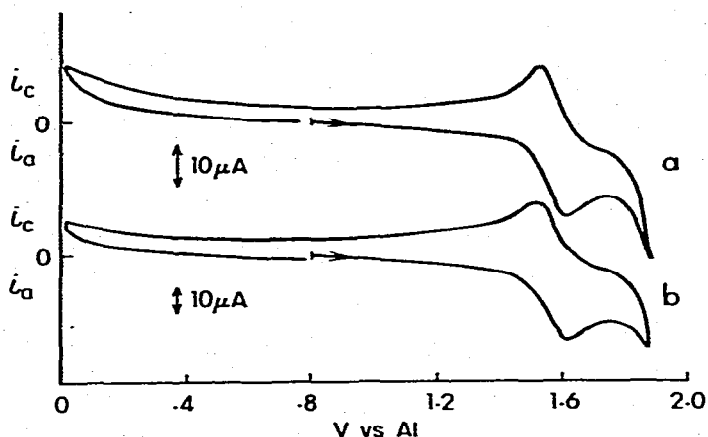
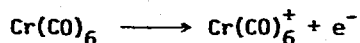


Figure 2 - Cyclic voltammograms of the solution described in Figure 1.

Scan rates: a) 0.1, and b) 0.5 V sec^{-1} .

tion is a reversible diffusion-controlled one-electron process at a vitreous carbon electrode:



Identical behavior was observed in acetonitrile by Pickett and Pletcher^{2,3}.

The electrochemical oxidation of Mo(CO)_6 and W(CO)_6 does not show such a simple pattern, as can be seen in Figure 3 and Figure 4 where cyclic voltammograms for the two compounds as a function of scan rate are shown. Both compounds exhibit one oxidation peak at 1.70 and 1.74 V vs Al reference electrode, respectively, at 0.1 V sec^{-1} rate. The oxidation peak potential moves anodically as the scan rate increases (30 - 40 mV/factor of 5 in scan rate). The cyclic voltammograms also display reduction peaks at 0.2 and 0.3 V vs. Al respectively, with a much smaller intensity. The ratio $i_p / v^{1/2}$ decreases ca. 20% from 0.1 to 0.5 V sec^{-1} , probably indicating the presence of follow-up chemical and electrochemical reactions to the initial electron transfer step⁹.

For both compounds no evidence was found for the formation of stable carbonyl cations. This fact is in accord with the greater tendency of these bulkier carbonyls to 7 coordination. Any cation formed would be prone to

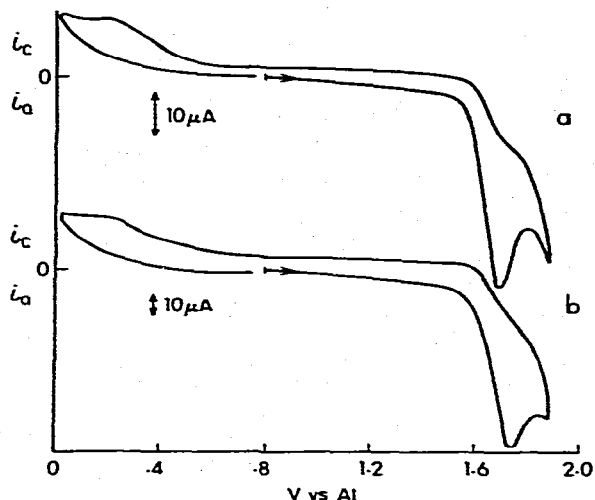
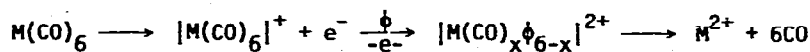


Figure 3 - Cyclic voltammograms of 1×10^{-3} M solution of $\text{Mo}(\text{CO})_6$ in the same medium described in Figure 1. Scan rate: a) 0.1, and b) 0.5 sec^{-1} .

nucleophilic attack. The solvent has a very large concentration of a nucleophilic agent, benzene ($X \sim 0.6$)¹⁰, which can displace CO.

It is likely that these carbonyl compounds are oxidized by a total $2e^-$ process, which is coupled to chemical reactions involving substitution of CO by benzene molecules:



This mechanism is analogous to that proposed by Pickett and Pletcher³ for the electrochemical oxidation of these compounds in acetonitrile.

It is interesting to compare peak potentials for oxidation of these 6B group metals in this solvent and acetonitrile. In the melt-benzene solution the oxidation peak potentials are: 1.61, 1.70 and 1.74 (0.1 sec^{-1}), respectively for Cr, Mo and W, where as in acetonitrile these compounds all show an oxidation peak potential at 1.53 V vs. sce. Even though the potentials for Mo and W refer to largely irreversible electrode reactions, it is very interesting to note that there is a 130 mV spread of potentials in this series in the 2:1 AlCl_3 :EtpyBr melt and benzene mixture. The similarity of potentials in acetonitrile was explained in terms of the removal of an

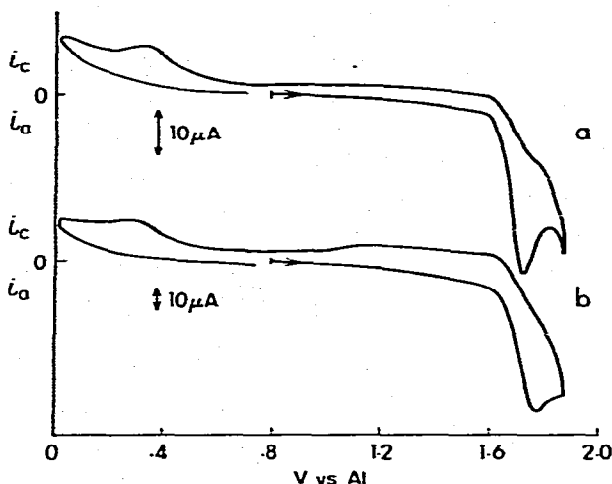


Figure 4 - Cyclic voltammograms of 1×10^{-3} M solution of $W(CO)_6$ in the same medium described in Figure 1. Scan rates: a) 0.1, and b) 0.5 $V \text{ sec}^{-1}$.

electron from an antibonding orbital³. The similarity of potentials implies that this energy level is not greatly dependent on the central metal atom³. In the melt-benzene medium the major Lewis acid species is the complex $AlCl_3 \cdot \phi (X \sim 0.1)^{10}$ which exchanges coordinated benzene very fast with solvent molecules¹⁰. It is conceivable that this spread of potentials is associated with an interaction between carbonyl ligands and the Lewis acid $AlCl_3$. This coordination would affect both σ and π bonding abilities of CO, decreasing the first but significantly increasing the second. The charge on the metal ion should then increase as the π back-donating ability of the metal increases. Following this argument, the oxidation potentials should increase in the order: $Cr < Mo < W$, which agrees with the observed experimental order.

The electrochemical oxidation of $Fe(CO)_5$ is very interesting. The oxidation peak is found at 1.08 V vs. Al reference electrode in the cyclic voltammograms shown in Figure 5. The peak potentials do not shift with scan rate within the experimental error. The ratio $i_{pa}/v^{1/2}$ is essentially constant, but the ratio i_{pa}/i_{pc} is smaller than unity. The reduction peak moves with scan rate and is separated from the oxidation peak by only -.14

0.22 V (0.1 - 0.5 V/sec), as compared to 1.4 - 1.5 V for the W and Mo derivatives.

A normal pulse voltammogram of $\text{Fe}(\text{CO})_5$ in the 2:1 AlCl_3 :EtpyBr melt and benzene medium is shown in Figure 6. The $\log i/i_d - i$ vs E plot is linear with a 55 ± 2 mV slope, indicating a one-electron reversible process with a half-wave potential of 1.02 V vs. Al reference electrode.

These data place the electrochemical behavior of $\text{Fe}(\text{CO})_5$ between that of $\text{Cr}(\text{CO})_6$ and $\text{Mo}(\text{CO})_6$ or $\text{W}(\text{CO})_6$. They also indicate that the cation $\text{Fe}(\text{CO})_5^+$ has some stability in this solvent system, which was not observed in acetonitrile³.

It is also important to notice that iron pentacarbonyl is much more easily oxidized than all other carbonyl compounds studied. Table 1 assembles all observed peak potentials for the metal carbonyls studied here, and also compares these potentials with those determined by Pickett

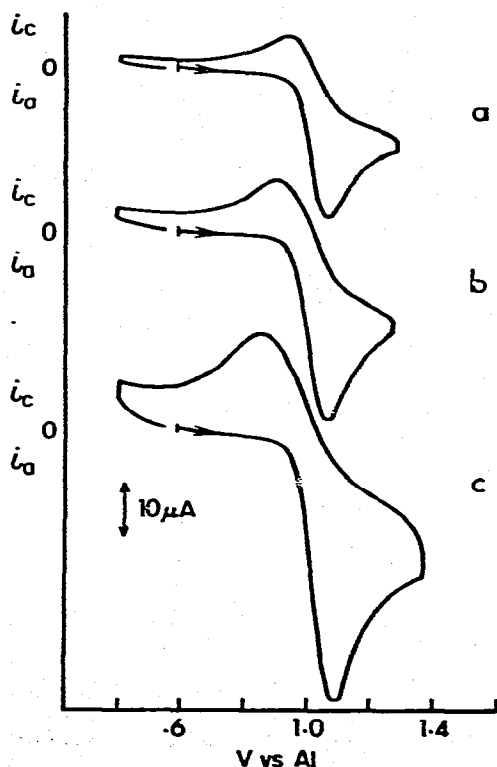


Figure 5 - Cyclic voltammograms of 1×10^{-3} M solution of $\text{Fe}(\text{CO})_5$ in the same medium described in Figure 1. Scan rates: a) 0.1, b) 0.2, and c) 0.5 V sec^{-1} .

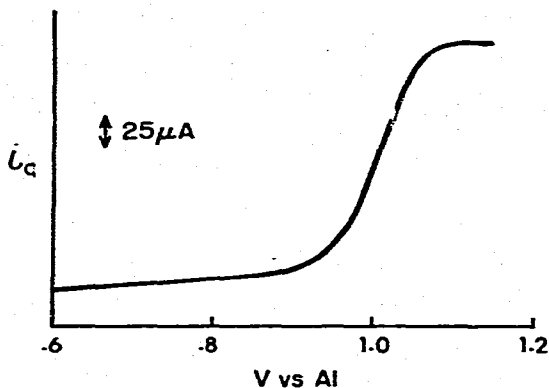


Figure 6 - Normal pulse voltammogram of 1×10^{-3} M solution of $\text{Fe}(\text{CO})_5$ in the same medium described in Figure 1.

and Pletcher³. A curious feature of the table is that the separation between anodic and cathodic peak potentials for Mo (W) is ca. 0.5 V is larger in acetonitrile than in the melt system.

The ease of oxidation of $\text{Fe}(\text{CO})_5$ in the melt-benzene medium can also be attributed to a strong interaction between the metal carbonyl and Lewis acid species in the melt. It is conceivable that this interaction can give rise to a symmetry distortion of $\text{Fe}(\text{CO})_5$. There, the HOMO which is non-bonding originally, can have its energy raised as a result of symmetry distortion, which would tend to make the oxidation easier.

The half-wave potentials for $\text{Cr}(\text{CO})_6$ and $\text{Fe}(\text{CO})_5$ can be better compared and interpreted as standard electrode potentials¹¹. The potentials are 1.52 and 1.02 respectively. There is a correlation between the standard potential and the charge of the carbonyl entity in an isoelectronic series. For instance, the redox couples: $\text{V}(\text{CO})_6^+/\text{V}(\text{CO})_6$, $\text{Cr}(\text{CO})_6^+/\text{Cr}(\text{CO})_6$ and $\text{Mn}(\text{CO})_6^+/\text{Mn}(\text{CO})_6$ show standard potentials of -0.05, +1.50 and +3.00 V vs. sce³. As positive charge is added to the system, the oxidation becomes more difficult. In the present study, one can conclude that the charge of the carbonyl entity is larger for the chromium than for the iron derivative.

Finally, the electrochemical oxidation of the binuclear metal carbonyls $\text{Mn}_2(\text{CO})_{10}$ and $\text{Re}_2(\text{CO})_{10}$ is shown in Figure 7. Only one anodic current peak

TABLE I

Anodic peak potentials for metal carbonyls in mixtures of 2:1 aluminum chloride:ethylpyridinium bromide and benzene (50% v/v) (present work) and acetonitrile (from Reference 3). Scan rate 0.1 V sec^{-1} , at $28 \pm 3^\circ\text{C}$.

Compound	PRESENT WORK			IN ACETONITRILE		
	E_{Pa} V vs. Al	E_{Pc} V vs. Al	Δ	E_{Pa} V vs. Sce	E_{Pc} V vs. Sce	Δ
$\text{Cr}(\text{CO})_6$	1.61	1.54	0.07	1.53	1.47	0.06
$\text{Mo}(\text{CO})_6$	1.70	.20	1.50	1.53	-.32	1.97
$\text{W}(\text{CO})_6$	1.74	.32	1.42	1.53	-.44	1.85
$\text{Fe}(\text{CO})_5$	1.08	.94	.14	1.51	not listed	

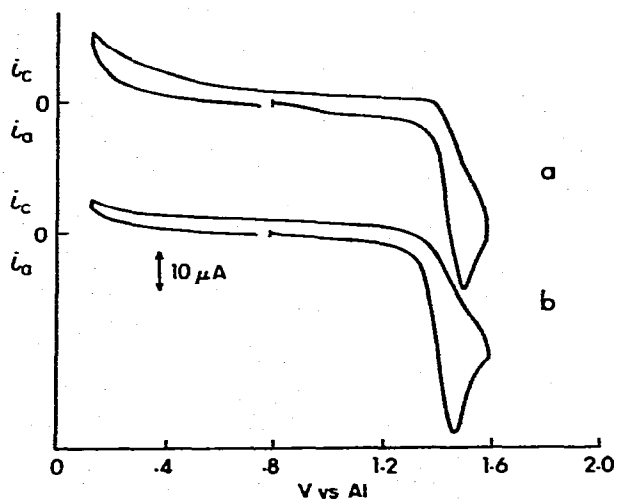


Figure 7 - Cyclic voltammograms of $1 \times 10^{-3} \text{ M}$ dinuclear carbonyls $\text{Re}_2(\text{CO})_{10}$ (a) and $\text{Mn}_2(\text{CO})_{10}$ (b) at 0.1 V sec^{-1} in the same medium described in Figure 1.

can be observed in the accessible potential range. Peak potentials at 1.47 and 1.50 V vs. Al were found. It is not surprising that in the melt the reduction corresponding to decomposition products was not observed. Pickett and Pletcher³ observed oxidation peaks at 1.55 V vs. sce in acetonitrile for these carbonyls. The reduction peaks were found at -1.32 and -1.12 V vs. sce respectively. Even considering that peak potential separation in the melt is ca. 0.5 V smaller than in acetonitrile, those potentials would be beyond the cathodic limit of the melt corresponding to aluminum deposition.

CONCLUSION:

The electrochemical oxidation of the metal carbonyls $M(CO)_6$ | $M = Cr, Mo, W$ |, $Fe(CO)_5$ and $M_2(CO)_{10}$ | $M = Mn, Re$ | was studied in a medium of high Lewis acidity composed of an aluminum chloride-ethylpyridinium bromide (2:1 molar acid) melt and benzene (50% v/v). The seventeen electron cation $Cr(CO)_6^+$ was found to be stable in this medium. Some stability was also found for the analogous iron pentacarbonyl derivative. Peak potentials in this medium are widely separated pointing towards an interaction between the carbonyl ligands and the Lewis acid species in the solvent.

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