

Redox Properties of Iron Carbonyl Complexes

NABIL EL MURR* and ANNIE CHALOYARD

Received June 15, 1981

In different solvents at mercury, platinum, and carbon electrodes, polarography, cyclic voltammetry, and electrolyses of $\text{Fe}(\text{CO})_5$, $\text{Fe}_3\text{CO}_{12}$, and $[\text{HFe}(\text{CO})_4]^-$ were performed in both the absence and the presence of a controlled amount of water. In the absence of water, $\text{Fe}(\text{CO})_5$ in either tetrahydrofuran (THF) or ethanol (EtOH) is electrolytically reduced into $[\text{Fe}_2(\text{CO})_8]^{2-}$ no matter what the electrode material. The electron-transfer process is always monoelectronic. In the presence of water, two electrons are involved in the reduction of $\text{Fe}(\text{CO})_5$, which forms $[\text{HFe}(\text{CO})_4]^-$. The electrochemical behavior of $\text{Fe}_3\text{CO}_{12}$ was also examined. In THF, $\text{Fe}_3\text{CO}_{12}$ decomposes. In CH_2Cl_2 two reduction steps are observed, corresponding with the formation of the mono- and dianion. The dianion is chemically and electrochemically unstable while the first electron-transfer process is electrochemically reversible. In the time scale of electrolysis, the monoanion is not stable; it decomposes into $\text{Fe}(\text{CO})_5$ and other carbonyl complexes. No change in the electrochemical behavior of $\text{Fe}_3\text{CO}_{12}$ is observed when experiments are performed in the presence of water. The electrochemical behavior of $[\text{HFe}(\text{CO})_4]^-$ depends on the nature of the solvent. At a platinum electrode and in the absence of water, oxidation is monoelectronic. In the presence of a base and water, three electrons are involved in the oxidation process of $[\text{HFe}(\text{CO})_4]^-$.

Introduction

The carbonyl complexes of iron, the related anions, and their corresponding protonated species occupy an important position in coordination chemistry. More particularly, the mononuclear members of this series have been the subject of extensive studies. $\text{Fe}(\text{CO})_5$, $\text{Fe}(\text{CO})_4^{2-}$, and $\text{HFe}(\text{CO})_4^-$ have found important applications in organic and organometallic synthesis. Many iron carbonyl complexes have been used as homogeneous catalysts or precursors to active catalytic species. Currently, much attention is focused on an interesting variation of the "oxo" process in which 2 mol of carbon monoxide plus water is used instead of carbon monoxide and hydrogen for the reductive addition of CO to an olefin to yield aldehydes and then alcohols. The first catalyst used in such a system was iron pentacarbonyl.¹ Many other carbonyl complexes are now known to be active in this water-gas shift reaction.²⁻⁴ It seems that the solutions obtained by treating iron carbonyl complexes with aqueous alkali function as a reducing system without intermediate formation of molecular hydrogen;¹ thus the carbonyl complex could proceed in such systems by transfer of electrons at least for the generation of the active species. That is why it seemed important to us to study first the redox behavior of some iron carbonyl complexes and to examine later their activity in the conditions of the water-gas shift reaction, in order to discover whether this reaction could be activated electrochemically and whether, with use of the electrochemical techniques, the active could be identified. We report now the first part of this study, which concerns the redox behavior of $\text{Fe}(\text{CO})_5$, $\text{Fe}_3\text{CO}_{12}$, and $[\text{HFe}(\text{CO})_4]^-$.

Experimental Section

Materials. Tetrahydrofuran (Fluka) was purified by fractional distillation under a stream of argon from sodium-benzophenone. Ethanol (Prolabo R.P. quality, containing less than 0.2% H_2O) was used without further purification. The supporting electrolyte $(\text{Bu}_4\text{N})^+(\text{PF}_6)^-$ (Fluka) was deoxygenated and dehydrated by melting under vacuum. The metal carbonyls $\text{Fe}(\text{CO})_5$ and $\text{Fe}_3\text{CO}_{12}$ (Alfa) were used without purification. $[\text{HFe}(\text{CO})_4]^-$ (PPN)⁺ was prepared by a standard procedure.

Apparatus. Electrochemical experiments were carried out in a three-electrode cell. The reference and auxiliary electrodes were separated from the solution by a tube with a glass frit in its extremity, containing the electrolytic solvent and the supporting electrolyte. For the polarographic measurement, the working electrode was a drop-

ping-mercury electrode with a dropping time of 0.5 s. For the cyclic voltammetry studies the working electrode was a Pt or glassy carbon disk. Coulometry and preparative experiments were carried out in a similar three-compartment cell. The working electrode was a 50-cm³ mercury pool, 35-cm³ platinum plate, or 35-cm³ carbon gauze. The working electrode compartment contained 40 cm³ of solution, which was stirred with a magnetic stirrer. In all solvents, the reference electrode was an aqueous standard calomel electrode (SCE) and the auxiliary electrode a platinum wire.

All electrochemical measurements were carried out under an argon atmosphere. Polarography and cyclic voltammetry were performed with Tipol and EPL2 Tacussel instruments; coulometry and preparative electrolyses were performed with an Amel Model 552 potentiostat. An inlet with a silicon rubber septum allowed samples to be taken with a syringe and to be examined by IR spectroscopy with a Beckman IR 7 spectrophotometer.

Results and Discussion

The electrochemical behavior of iron carbonyl complexes has been studied by several authors,⁵⁻¹² and different results were obtained. The nature of the solvent and electrode material used were proposed to be responsible in obtaining these contrasting results.¹⁰ That is why we studied the polarography, cyclic voltammetry, and electrolysis of $\text{Fe}(\text{CO})_5$, $\text{Fe}_3\text{CO}_{12}$, and $[\text{HFe}(\text{CO})_4]^-$ in different solvents, at mercury, platinum, and glassy carbon electrodes, in the absence and in the presence of a controlled amount of water. We think that our results could be summarized as follows.

$\text{Fe}(\text{CO})_5$. In tetrahydrofuran (THF) with $(\text{Bu}_4\text{N})^+(\text{PF}_6)^-$ as the supporting electrolyte, the polarogram (dropping-mercury electrode) of $\text{Fe}(\text{CO})_5$ exhibits only one cathodic wave at -1.77 V vs. SCE. No anodic wave is detected in this solvent at the mercury electrode. The cyclic voltammetry at platinum or at a glassy carbon electrode, at a scan rate of 0.1 V s⁻¹, shows two peaks of equal height, one cathodic at -2.0 V and one anodic at +1.5 V. Both correspond to nonreversible electron-transfer processes. In THF at a mercury electrode (polarography) or at a platinum electrode (cyclic voltammetry), the current for unit concentration for the reduction of $\text{Fe}(\text{CO})_5$ is almost exactly the same as that for the known one-electron oxidation process of ferrocene. The presence of

(1) For a review see, for example, R. Pettit, C. Mauldin, T. Cole, and H. Kang, *Ann. N.Y. Acad. Sci.*, **295**, 151 (1977).
 (2) H. Kang, C. Mauldin, T. Cole, W. Steiger, C. Cann, and R. Pettit, *J. Am. Chem. Soc.*, **99**, 8323 (1977).
 (3) R. M. Laine, *J. Am. Chem. Soc.*, **100**, 6451 (1978).
 (4) R. B. King, C. C. Frazier, R. M. Hanes, and A. D. King, Jr., *J. Am. Chem. Soc.*, **100**, 2925 (1978).

(5) R. E. Dessy, F. E. Stary, R. B. King, and M. Waldrop, *J. Am. Chem. Soc.*, **88**, 471 (1966).
 (6) C. J. Pickett and D. Pletcher, *J. Chem. Soc., Dalton Trans.*, 879 (1975).
 (7) C. J. Pickett and D. Pletcher, *J. Organomet. Chem.*, **102**, 327 (1975).
 (8) C. J. Pickett and D. Pletcher, *J. Chem. Soc., Dalton Trans.*, 636 (1976).
 (9) A. A. Vlcek, *Nature (London)*, **177**, 1043 (1956).
 (10) A. M. Bond, P. A. Dawson, B. M. Peake, B. H. Robinson, and J. Simpson, *Inorg. Chem.*, **16**, 2199 (1977).
 (11) D. Mikolova, J. Klima, and A. A. Vlcek, *Inorg. Chim. Acta*, **27**, L67 (1978).
 (12) S. W. Blanch, A. M. Bond, and R. Colton, *Inorg. Chem.*, **20**, 755 (1981).

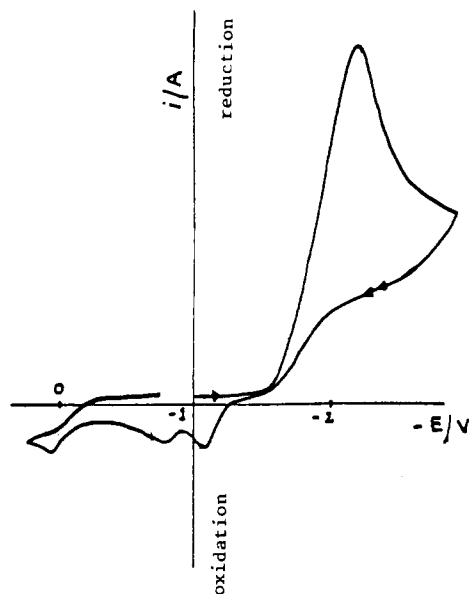
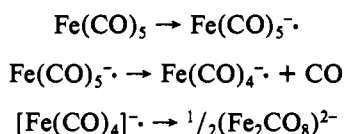


Figure 1. Cyclic voltammogram at 20 °C of 10^{-3} M $\text{Fe}(\text{CO})_5$ at a Pt electrode (scan rate 100 mV s^{-1}) in tetrahydrofuran.

additional anodic peaks in the reverse scan of the voltammogram suggests that chemical reactions occur after the oxidation at the electrode of $\text{Fe}(\text{CO})_5$ (Figure 1). Electrolysis of $\text{Fe}(\text{CO})_5$ solution on a mercur pool, at the potential of the cathodic wave, requires 1 faraday/mol of $\text{Fe}(\text{CO})_5$ and produces a red-orange solution, that does not show any cathodic or anodic peak but exhibits two peaks at 1905 and 1860 cm^{-1} in its infrared spectrum. The absence after electrolysis of the anodic peaks observed in the reverse scan of the voltammogram of $\text{Fe}(\text{CO})_5$ shows that these peaks correspond to the oxidation of unstable intermediate species such as $\text{Fe}(\text{CO})_4^-$.

Our electrochemical results in THF using mercury as the working electrode are fully consistent with Scheme I.

Scheme I



The same results were obtained when THF solutions of $\text{Fe}(\text{CO})_5$ were reduced on platinum or carbon electrodes. They are in agreement with those recently reported by Krusic et al.¹³ They demonstrated that the chemical reduction of $\text{Fe}(\text{CO})_5$ at -80 °C leads to the generation of four different paramagnetic species. The reaction of $\text{Fe}(\text{CO})_5$ with 1 equiv of sodium naphthalide in THF at ambient temperature gives good yields of $\text{Fe}_2(\text{CO})_8^{2-}$, which could be contaminated by a trace amount of the paramagnetic species $\text{Fe}_2(\text{CO})_8^-$. Treatment of $\text{Fe}(\text{CO})_5$ with 2 equiv of sodium naphthalide produces $\text{Na}_2\text{Fe}(\text{CO})_4$ in excellent yields. The same result was obtained by Dawson et al.¹⁴ when $\text{Fe}(\text{CO})_5$ was reduced by Na.

Concerning the oxidation of $\text{Fe}(\text{CO})_5$ at platinum or glassy carbon electrodes, we believe, as was suggested by Pickett and Pletcher,^{6,8} that the monoelectronic oxidation step leads to the generation of the corresponding cation, which decomposes. The ultimate product could be then Fe^{2+} or Fe^{3+} .

In THF plus 2.5% water, the polarogram at the dropping-mercury electrode is the same as above. No change could be

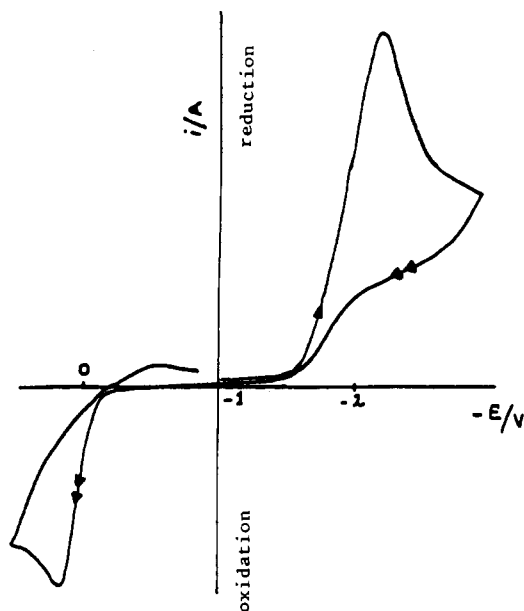


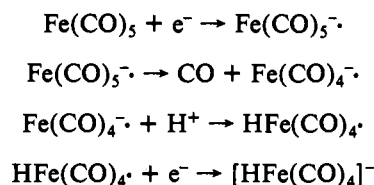
Figure 2. Cyclic voltammogram at 20 °C of 10^{-3} M $\text{Fe}(\text{CO})_5$ at a Pt electrode (scan rate 100 mV s^{-1}) in tetrahydrofuran + 2.5% water.

noticed concerning either the potential or the height of the cathodic wave. Cyclic voltammetry indicates no change in the characteristics of the cathodic peak but rather the formation, after reduction, of a new species, which exhibits an anodic peak at $+0.12 \text{ V}$ (Figure 2).

Electrolysis of $\text{Fe}(\text{CO})_5$ solution in the presence of water requires 2 faradays/mol and leads to a solution that, in its cyclic voltammogram (glassy carbon electrode), exhibits a peak at $+0.12 \text{ V}$. In its infrared spectrum, peaks are observed at 1920 and 1890 cm^{-1} . Electrolysis at platinum and in the presence of water was not possible, but similar results were obtained when electrolysis was performed on a carbon electrode. The electrochemical behavior of $\text{Fe}(\text{CO})_5$ in the presence of water is consistent with an ECE mechanism.

Infrared and electrochemical studies performed on an authentic sample of $[\text{HFe}(\text{CO})_4]^-$ are in agreement with Scheme II.

Scheme II



The electrochemical behavior of $\text{Fe}(\text{CO})_5$ was also studied in ethanol at mercury, platinum, or glassy carbon electrodes. In the presence of $(\text{Me}_4\text{N})^+(\text{Cl})^-$ as electrolyte support, $\text{Fe}(\text{CO})_5$ shows in its polarogram one monoelectronic cathodic wave at -1.64 V vs. SCE. Electrolysis confirmed the 1-faraday process. In the presence of 2.5% water, the same results were obtained as was observed in THF. In the absence of water, the electrolytic reduction of $\text{Fe}(\text{CO})_5$ is a monoelectronic process whatever the solvent used. This process becomes bielectronic when water is present as well as when the solvent is not free of water.

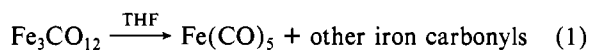
$\text{Fe}_3\text{CO}_{12}$. In a fresh THF solution of $\text{Fe}_3\text{CO}_{12}$, the polarogram (dropping mercury electrode, $(\text{Bu}_4\text{N})^+(\text{PF}_6)^-$ supporting electrolyte) shows two well-defined cathodic waves, A and B, at -0.32 and -0.97 V and two other ill-defined waves, C and D, at more cathodic potentials. When the solution was stirred at room temperature, A and B decrease while C and D increase. After about 1 h the polarogram shows only the

(13) (a) P. J. Krusic, J. S. Filippo, Jr., B. Hutchinson, R. L. Hance, and L. M. Daniels, *J. Am. Chem. Soc.*, **103**, 2129 (1981); (b) P. J. Krusic, *ibid.*, **103**, 2131 (1981).

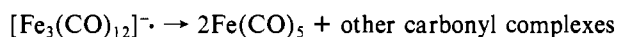
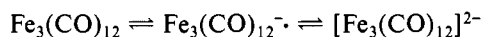
(14) P. A. Dawson, B. M. Peake, B. H. Robinson, and J. Simpson, *Inorg. Chem.*, **19**, 465 (1980).

two cathodic waves D and C. D is well-defined at -1.76 V, and C is ill-defined and situated at approximately -2.2 V. At this point it became possible to identify the wave C as the one of $\text{Fe}(\text{CO})_5$. This was also confirmed by infrared spectroscopy.

The decomposition of $\text{Fe}_3\text{CO}_{12}$ in THF (eq 1) has prompted



us to study the electrochemical behavior of $\text{Fe}_3\text{CO}_{12}$ in CH_2Cl_2 . Here, the polarogram shows two well-defined waves of equal heights at -0.41 and -0.84 V. Cyclic voltammetry shows that both processes are reversible at a scan rate of 0.1 V s^{-1} . For scan rates lower than 0.1 V s^{-1} the second process becomes less reversible. The appearance of additional peaks in the reverse scan of the voltammogram suggests that the $[\text{Fe}_3(\text{CO})_{12}]^{2-}$ unit is not stable and decomposes very rapidly. Electrolysis at a mercury pool, at the level of the first wave, requires 1 faraday/mol. However, the cathodic wave at -0.4 V does not become anodic: a peak at $+1.5$ V is observed in the cyclic voltammogram and corresponds to the formation of $\text{Fe}(\text{CO})_5$. This shows that the first electron transfer involving $\text{Fe}_3\text{CO}_{12}$ is electrochemically but not chemically reversible. $(\text{Fe}_3\text{CO}_{12})^-$ is not stable and decomposes, giving 2 mol of $\text{Fe}(\text{CO})_5$. The generation of $\text{Fe}(\text{CO})_5$ was confirmed by infrared spectroscopy and the stoichiometry of the reaction by the comparison of the heights of the peaks in the cyclic voltammograms performed before and after electrolysis. These observations are compatible with those reported by Dawson et al.¹⁴



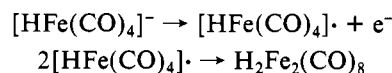
It was impossible for us to identify the other carbonyl complexes formed besides $\text{Fe}(\text{CO})_5$ after the electrolytical reduction of $\text{Fe}_3(\text{CO})_{12}$ at room temperature. We observed a single line at $g = 2.050$ in the ESR spectrum of the electrolytical solution. This is consistent with the studies done by Dawson et al.,¹⁴ who reduced $\text{Fe}_3\text{CO}_{12}$ at different temperatures, attributing this signal to the product arising from the decomposition of $(\text{Fe}_3\text{CO}_{12})^-$. This decomposition product could be $\text{Fe}_3(\text{CO})_{11}^-$, which was identified by Krusic et al.¹³ and which is characterized by a single ESR signal ($g = 2.0497$). When electrolysis is performed at the level of the second cathodic wave, 2 faradays is consumed. Cyclic voltammetry and IR show the formation of some $\text{Fe}(\text{CO})_5$ in addition to other carbonyl complexes. The IR spectrum then shows four important peaks at 2022, 1995, 1933, and 1900 cm^{-1} .

When water is added to a CH_2Cl_2 solution of $\text{Fe}_3\text{CO}_{12}$ and electrolysis is performed on the level of the first wave, similar results to those obtained in the absence of water are noticed. This leads to the conclusion that $[\text{Fe}_3(\text{CO})_{12}]^{2-}$ does not extract a proton from water, and no hydride species such as $[\text{HFe}_3(\text{CO})_{11}]^-$ are formed. Once again, the same results are obtained if electrolyses are performed on platinum or carbon

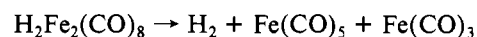
electrodes. No participation of the electrode material or of the solvent occurs during the electron transfer into $\text{Fe}_3\text{CO}_{12}$.

[HFe(CO)₄]⁻PPN⁺. At the dropping-mercury electrode, the polarogram of the THF solution of $[\text{HFe}(\text{CO})_4]^- (\text{PPN})^+$ shows two anodic waves at -0.07 and -0.43 V and cathodic waves at -2.06 and -2.23 V, which correspond to the reduction of PPN^+ . Cyclic voltammetry on a platinum electrode shows only one irreversible anodic peak at $+0.12$ V. This indicates a participation of the mercury electrode in the oxidation process. Therefore, the two anodic waves at -0.07 and -0.043 V correspond to the mercury oxidation in the presence of $[\text{HFe}(\text{CO})_4]^-$.

Electrolysis was only performed on platinum to avoid the oxidation of the mercury electrode. The electrolytical oxidation takes place with consumption of 1 faraday/mol of $[\text{HFe}(\text{CO})_4]^-$ and produces a redish solution that exhibits several peaks in its IR spectrum. Two of them could be identified as those of $\text{Fe}(\text{CO})_5$. The monoelectronic oxidation of $[\text{HFe}(\text{CO})_4]^-$ may be consistent with the reaction



$\text{H}_2\text{Fe}_2(\text{CO})_8$ decomposes, leading to $\text{Fe}(\text{CO})_5$ and some other iron carbonyls in a way similar to that described by Hieber and Vetter as the decomposition process for $\text{H}_2\text{Fe}(\text{CO})_4$.¹⁵



When water is added to a fresh solution of $[\text{HFe}(\text{CO})_4]^-$, cyclic voltammetry shows that the oxidation peak increases in height while its potential is still the same. This is consistent with an ECE mechanism whereby the newly formed species is more easily oxidized than the starting material. The water in this reaction could be a source of either protons or OH^- . To solve this problem, we compared the cyclic voltammograms of solutions of $[\text{HFe}(\text{CO})_4]^-$ in both the presence and the absence of proton donors such as phenol. We noticed no change in the height of the anodic peak at $+0.12$ V. Electrolysis in the presence of PhOH consumes only 1 faraday/mol of $[\text{HFe}(\text{CO})_4]^-$. In contrast, when water and triethylamine were added to a fresh solution of $[\text{HFe}(\text{CO})_4]^-$ in THF, a drastic change in the height of the anodic peak occurred, and electrolysis showed that 3 faradays were consumed per molecule of $[\text{HFe}(\text{CO})_4]^-$. This is consistent with an ECE mechanism in which OH^- reacts with $[\text{HFe}(\text{CO})_4]^-$. We think that different schemes may illustrate these electrochemical results. No complex was isolated, and only speculations can be made for the moment. However, we must stress the great importance of the effect of OH^- in this electron-transfer mechanism.

Registry No. $\text{Fe}(\text{CO})_5$, 13463-40-6; $\text{Fe}_3(\text{CO})_{12}$, 17685-52-8; $[\text{PPN}][\text{HFe}(\text{CO})_4]$, 56791-54-9; $[\text{Fe}_2(\text{CO})_8]^{2-}$, 25463-33-6.

(15) W. Hieber and H. Vetter, *Z. Anorg. Allg. Chem.*, **212**, 145 (1933).