2380 Organometallics 1993, 12, 2380–2382

Infrared Spectroelectrochemical Observation of the Reduction of Iron Pentacarbonyl

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Received December 4, 1992

Summary: The electrochemical reduction of iron pentacarbonyl was studied using infrared spectra collected simultaneously with the electrochemical conversion. Evidence for a mechanism proceeding through the iron tetracarbonyl dianion is observed.

Introduction

One of the earliest studies[1] of the reduction of iron pentacarbonyl (I) concluded, from infrared evidence, that the reduction of I was a one-electron process leading to the formation of $[Fe_2(CO)_8]^{2-}$ (II). Later investigations[2] confirmed this result and assumed that II was formed from the dimerization of two molecules of $[Fe(CO)_4]^{\bullet-}$ resulting from the reduction of I. It is clear that the chemical reactions following initial electron transfer are rapid and chemically irreversible. The intermediate species formed have been used in reactions with phosphines[3,4] to produce substituted derivatives.

The most recent study[5] used high sweep rates at ultramicroelectrodes to investigate the reduction process. It was found that while a one-electron process occurred at sweep rates below 1000 mV s^{-1}, the number of electrons transferred per mole increased toward a limit of 2 at high sweep rates. By determining the redox potentials of $[Fe(CO)_4]^{2-}$ (III) and the dianion II, using cyclic voltammetry, the authors concluded that the following scheme is consistent with these and other observations:

$$\underset{\textbf{I}}{Fe(CO)_5} + e^- \rightarrow Fe(CO)_5^{\bullet-}$$

$$Fe(CO)_5^{\bullet-} \rightarrow Fe(CO)_4^{\bullet-} + CO$$

$$Fe(CO)_4^{\bullet-} + e^- \rightarrow \underset{\textbf{III}}{Fe(CO)_4^{2-}}$$

$$\underset{\textbf{III}}{Fe(CO)_4^{2-}} + \underset{\textbf{I}}{Fe(CO)_5} \rightarrow \underset{\textbf{II}}{Fe_2(CO)_8^{2-}} + CO$$

$$\underset{\textbf{III}}{Fe(CO)_4^{2-}} + H^+ \rightarrow \underset{\textbf{IV}}{HFe(CO)_4^-}$$

In the above scheme the generation of $Fe(CO)_4^{2-}$ (III) is a rapid process. III is then capable of reacting with I to give II and carbon monoxide, or it may react with acidic protons to produce the hydride anion IV. These conclusions were in direct disagreement with earlier papers[1,2] that stated II was produced by the dimerization of two iron pentacarbonyl radical anions.

The aim of the present study was to use infrared monitoring of the transformations occurring during a cathodic potential sweep of a solution of iron pentacarbonyl and thereby provide direct evidence for the nature of the reduction processes. This work was accomplished with a spectroelectrochemical cell developed and described elsewhere[6] which uses a gold-minigrid electrode mounted on the surface of the prism of an internal reflection cell.

Results and Discussion

The cyclic voltammogram for a cathodic sweep at 50 mV/s between 0 and −2500 mV is shown in Figure 1. A large chemically irreversible reduction wave is seen at −2100 mV. The back sweep shows three anodic waves at −1280, −960, and −120 mV. This cyclic voltammogram is consistent with other reports[1–3,5,7] of cathodic sweep experiments in the literature. The first two anodic waves are known to increase in relative magnitude at faster scan rates, indicating that these products from the reduction step are not particularly stable. These two oxidation waves on the back sweep are believed[5] to belong to the oxidation of $Fe_2(CO)_8^{2-}$ (II) and $Fe(CO)_4^{2-}$ (III).

The simultaneous FTIR data collected during the electrochemical experiments provide information on the nature of the species involved. Spectra taken during the reduction wave show the consumption of iron pentacarbonyl (I), as evidenced by negative bands at 2018 and 1993 cm^{-1}, and the appearance of an intense broad band centered at 1738 cm^{-1} (Figure 2). This band is almost certainly due to $Fe(CO)_4^{2-}$ (III). In a mull as the sodium salt III is reported[8] to exhibit a broad band at 1761 cm^{-1}. In DMF solution III appears[4] as a single broad band at 1730 cm^{-1}. Another paper[2] ascribes a strong broad band at 1720 cm^{-1} for the sodium cryptate salt in THF solution. Also evident are small bands at 1910, 1882, and 1867 cm^{-1}. Figure 3 represents the spectrum recorded at −2150 mV during the anodic portion of the sweep and shows the increased intensity of the three bands between 1910 and 1867 cm^{-1}. The intensity of the band at 1738 cm^{-1} has also increased due to the potential being closer to that required for the maximum electrode surface concentration of III. The bands at 1910 and 1867 cm^{-1} are in a constant ratio of approximately 0.6. As a result, the band at 1882 cm^{-1} must belong to another compound. These two compounds clearly result from the reaction of III, since when the potential shifts to a region (−600 mV) where I is no longer

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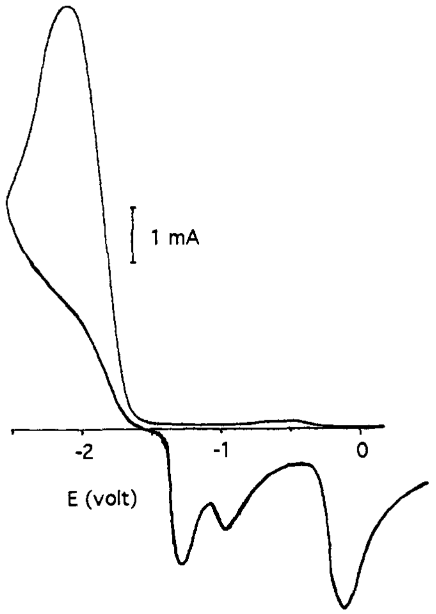

Figure 1. Cyclic sweep at 50 mV/s of 5 mM $Fe(CO)_5$ in THF recorded simultaneously with FTIR spectra.

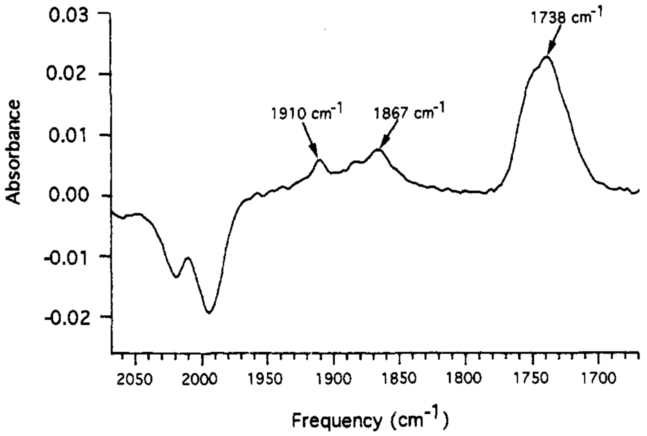

Figure 2. IR spectrum recorded between −1840 and −1960 mV during cathodic sweep.

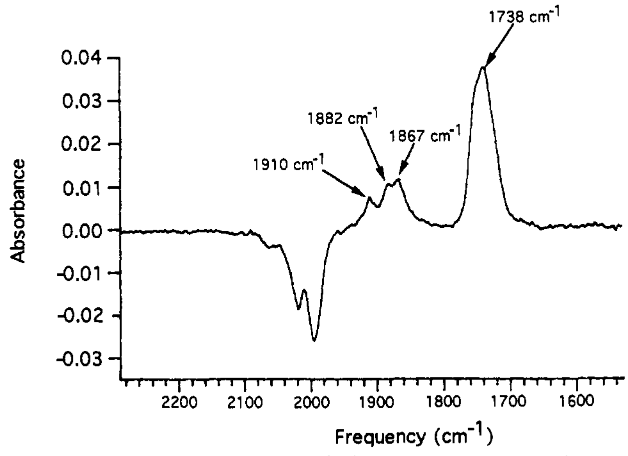

Figure 3. IR spectrum recorded between −2210 and −2090 mV during anodic sweep.

reduced, the absorbance at 1738 cm^{-1} disappears rapidly, while the other bands increase in intensity (Figure 4). The monitoring of the solution at about 15 μm from the electrode surface[6] means that III can be observed as long as its lifetime is sufficient for diffusion to the point of observation to occur. This is about 100 ms.

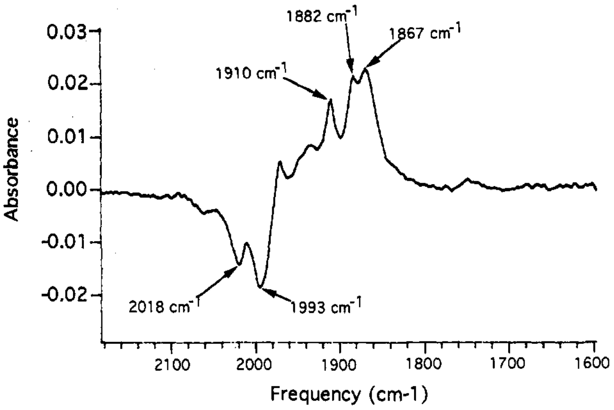

Figure 4. IR spectrum recorded between −660 and −540 mV during anodic sweep.

Table I. Band Assignments (cm^{-1}) for Observed Species

$Fe(CO)_5$ (I)	2018, 1993	$Fe(CO)_4^{2-}$ (III)	1738
$Fe_2(CO)_8^{2-}$ (II)	1910, 1868	$HFe(CO)_4^-$ (IV)	1881

Comparison of the spectra from a 10 mV/s sweep with those from the 50 mV/s sweep show that at slower scan rates the reaction of III has occurred to a greater extent for a given position in the cyclic sweep. This result is consistent with an electrochemical process followed by a chemical reaction, or an EC mechanism.

The bands at 1910 and 1867 cm^{-1} can be assigned to $Fe_2(CO)_8^{2-}$ (II) formed from the reaction of I and III. These bands were identified by comparison with literature[8] values. $HFe(CO)_4^-$ (IV) is reported[8] to show bands at 1914 (m) and 1880 (s) cm^{-1} and a weak band at 2008 cm^{-1}. The last band would not be seen against the large negative absorbance bands of I. A summary of the band assignments is provided in Table I. The highly basic nature of III allows the abstraction of a proton from trace water or from THF to compete with the reaction with I.

Conclusion

By using IR spectrometry to directly monitor the fate of the products generated by the electrochemical reduction of iron pentacarbonyl, it has been possible to provide direct evidence for the mechanism proposed by Amatore et al.,[5] which proceeds through an iron tetracarbonyl dianion intermediate.

Experimental Section

Tetrahydrofuran (THF) was distilled under argon from liquid sodium–potassium amalgam, while methylene chloride was distilled from calcium hydride under argon. All solutions were handled using Schlenk techniques under an atmosphere of argon. The argon was passed over a 30-cm column of heated BTS catalyst to remove any traces of oxygen, followed by columns of activated (24 h at 260 °C) 3-Å molecular sieves and phosphorus pentoxide to remove moisture. Finally the gas was bubbled through silicone oil to remove any small particles from the previous columns.

The supporting electrolyte, tetra-*n*-butylammonium hexafluorophosphate (Aldrich Chemical Co.), was dried under high vacuum in a round-bottom Schlenk flask connected to a rotary evaporator. The flask was heated with a 500 °F heat gun at a distance of about 15 cm for 4 h. The supporting electrolyte concentration was 0.2 M, which is close to the limit of solubilty in THF. The concentration of iron pentacarbonyl was 5 mM. For spectroelectrochemical analysis the solutions were placed in a Schlenk tube under argon and capped with a rubber septum.

To introduce the samples into the spectroelectrochemical cell,[6] a steel cannula, one end of which had been removed, was sealed to a Teflon flow line using small-diameter heat-shrink Teflon tubing. The tubing was shrunk by brief exposure to a Bunsen burner flame. The sharp end of the cannula was used to penetrate the septum, and the cell was flushed with a flow of argon from the side arm. The end of the cannula was then dipped into the solution, and flow was achieved from the gas pressure. To stop the flow, the excess pressure was vented.

The infrared spectra were collected using a Mattson Cygnus 100 FTIR equipped with a liquid-nitrogen-cooled MCT detector. All spectra were ratioed to the starting 5 mM solution of $Fe(CO)_5$ and supporting electrolyte in THF. When a scan rate of 50 mV/s was used, a 10-scan spectrum was collected in 2.5 s, meaning that each spectrum is the integrated response over a range of about 125 mV.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research program.

OM9207774