CAPSULES
notes and applications from Bioanalytical Systems, Inc.

Identification of the Products of Oxidation of $[CpFe(CO)_2]_2$ Using Infrared Spectroelectrochemistry

Purpose

There have been many electrochemical studies of the oxidative cleavage of the metal-metal bond in $[CpFe(CO)_2]_2$ (F1). It is generally accepted that the first step is the generation of the radical cation $[CpFe(CO)_2]_2^{+\cdot}$, but this intermediate has not been characterized. In this study, the radical cation and the products of the subsequent oxidation were identified by IR spectroscopy using controlled potential electrolysis in an OTTLE cell (F2) (1).

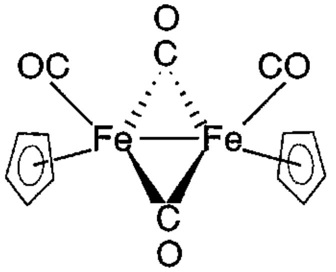

Figure 1. Structure of *cis* $[CpFe(CO)_2]_2$.

Reference

Electrochemistry and Infrared Spectroelectrochemistry of $[(\eta^5\text{-}C_5R_5)Fe(CO)_2]_2$ (R = H, Me): Generation and Characterization of $[(\eta^5\text{-}C_5R_5)Fe(CO)_2]_2(PF_6)$ Complexes, J. P. Bullock, M. C. Palazotto and K. R. Mann, Inorg. Chem. 30 (1991) 1284-1293.

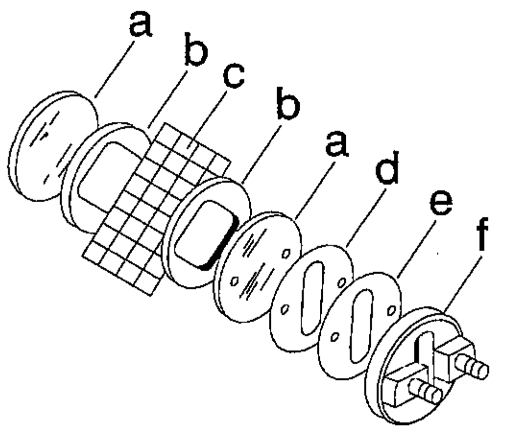

Figure 2. Diagram of an OTTLE cell. a) NaCl plates b) Tefzel gaskets c) gold minigrid electrode d) indium gasket e) Teflon gasket f) needle plate (1).

Methods

Cyclic voltammetry is a powerful technique for qualitative monitoring of the reactions of electrogenerated intermediates. However, it is not always possible to isolate these intermediates and their reaction products and characterize them by conventional methods, due to their reactivity. One way to circumvent these difficulties is to synthesize the intermediates by controlled potential electrolysis in an OTTLE cell (1) (Optically Transparent Thin Layer Electrode). As this cell is optically transparent, the electrolysis can occur in the spectrophotometer beam, and the redox processes can be monitored spectroscopically during electrolysis.

Results

The cyclic voltammogram of $[CpFe(CO)_2]_2$ in methylene chloride is shown in F3. The first oxidation is quasi-reversible. Controlled potential electrolysis at +1.1 V (vs Ag/AgCl) was followed by IR spectroscopy, and the spectra are shown in F4. The presence of isosbestic points indicates a clean conversion to the radical cation. The peaks of the neutral dimer are at 1773, 1955 and 1995 cm^{-1} and decrease during the electrolysis, and the peaks of the cation are at 1934, 2023 and 2055 cm^{-1}, and increase during electrolysis. The shift to higher wavenumbers is characteristic of a simple oxidation process.

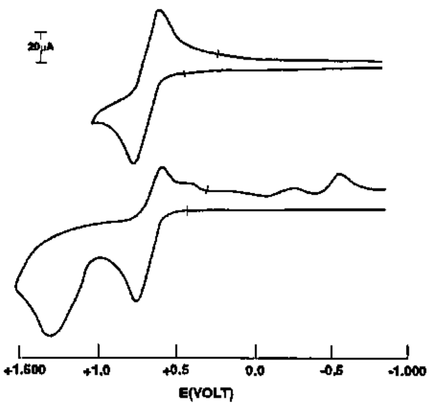

Figure 3. Cyclic voltammogram of $[CpFe(CO)_2]_2$. Potentials were measured with reference to Ag/AgCl.

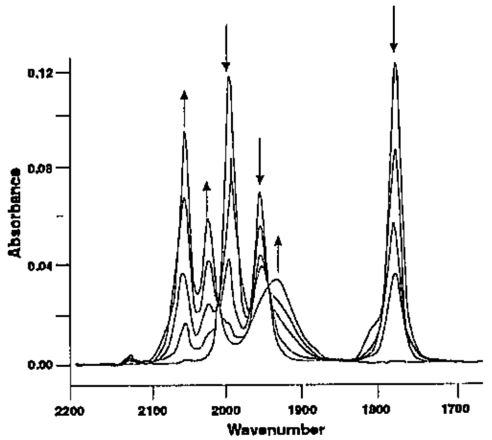

Figure 4. Infra-red spectral changes observed upon oxidation of a solution of $[CpFe(CO)_2]_2$ at +1.1 V.

The second oxidation is irreversible, and leads to products that are reduced at -0.27 and -0.57 V (F3). Controlled potential electrolysis at the second oxidation potential in the OTTLE cell showed the formation of $[CpFe(CO)_3]^+$ and $[CpFe(CO)_2(OH_2)]^+$, which were identified by comparison with the IR spectra and reduction potentials of actual samples. When the intermediate and products can be identified in this way, it provides a more certain basis for possible mechanisms.

Additional Reference

1) J. P. Bullock, D. C. Boyd and K. R. Mann, Inorg. Chem. 26 (1987) 3084-3086.