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A New Approach to Infrared Spectroelectrochemistry Using a Fiber-Optic Probe: Application to Organometallic Redox Chemistry

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Summary: A mid-IR fiber-optic cable operating as a "dip" probe has been used to obtain IR spectra of electrolysis solutions. The probe is employed in conventional electrochemical cells to sample the bulk of solution before, during, and after electrolysis. Unlike other spectroelectrochemical methods, this technique requires no cell design compromises which diminish the accuracy of the electrochemical data.

We report a new method for obtaining mid-infrared spectra of electrolysis products which has significant advantages over previously reported methods. A fiber-optic cable which is easily adapted to FTIR spectrometers is immersed in a conventional electrolysis cell and employed as a remote sensor. This method should enable IR spectroelectrochemistry to be applied to redox problems of increased complexity.

The difficulty of obtaining spectral information on molecules of limited stability is a major impediment to structural characterization of organometallic redox products.[1] IR spectroelectrochemistry is being increasingly used to address this problem.[2] When employed to monitor a thin layer of solution near the electrode surface, however, both reflectance and transmittance spectral methods involve inherent design compromises which limit the correlations one can make between the spectral and electrochemical responses. For example, the popular OTTLE (OTTLE = optically transparent thin-layer electrode) transmittance cell suffers from high ohmic loss, leading to errors in the control potential (E_{appl}) and severe distortion of voltammograms of electrolysis products.[3] These disadvantages have the effect of limiting the usefulness of the OTTLE cell for investigations of closely spaced waves and of slow chemical reactions coupled to electron transfer.

We sought a method which would take better advantage of the strengths of traditional multicompartment electrochemical cells and still allow *in situ* characterization of redox products by IR spectroscopy. Among those strengths are (1) accurate control of E_{appl}, (2) ability to quantitatively follow the progress of the electrolysis using a full complement of voltammetric methods, (3) good performance at low temperatures, and (4) rigorous exclusion of air from the electrolysis solution. To a standard electrolytic "H"-cell[4] we added only a fiber-optic ("dip") probe to obtain IR spectra. A Pt-gauze cylinder was employed to perform electrolyses, and Pt

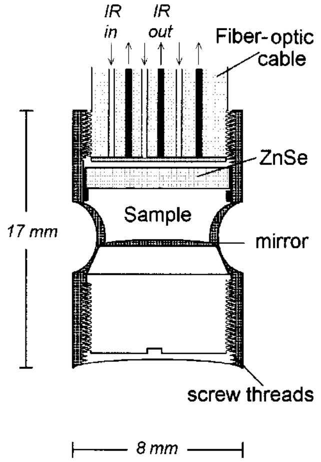

Figure 1. Schematic representation of the sampling probe head at the end of the fiber-optic cable. The portion shown is immersed in the electrolysis solution, and solution enters the sample chamber through holes in the stainless steel probe wall.

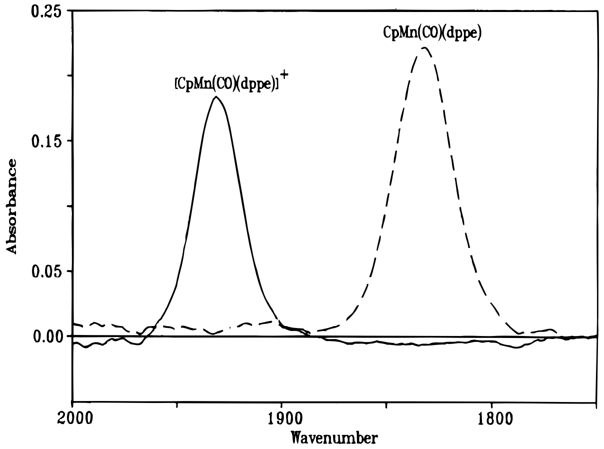

Figure 2. IR spectra in the carbonyl region before (dotted line) and after (solid line) one-electron anodic electrolysis of 1.0 mM CpMn(CO)(dppe) (**1**) in CH_2Cl_2/0.1 M $[NBu_4][PF_6]$ at 273 K.

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[1] Geiger, W. E. *Acc. Chem. Res.* **1995**, *28*, 351.

[2] Leading references: (a) Hill, M. G.; Rosenheim, L. D.; Mann, K. R.; Mu, X. H.; Schultz, F. A. *Inorg. Chem.* **1992**, *31*, 4108. (b) Brisdon, B. J.; Enger, S. K.; Weaver, M. J.; Walton, R. A. *Inorg. Chem.* **1987**, *26*, 3340. (c) Barley, M. H.; Anson, C. E.; Johnson, B. F. G.; Lewis, J. *J. Organomet. Chem.* **1988**, *339*, 151. (d) Best, S. P.; Clark, R. J. H.; Deeming, A. J.; McQueen, R. C. S.; Powell, N. I.; Acuna, C.; Arce, A. J.; De Sanctis, Y. *J. Chem. Soc., Dalton Trans.* **1991**, 1111. (e) Osella, D.; Feidler, J. *Organometallics* **1992**, *11*, 3875. (f) Moran, M.; Pascual, M. C.; Cuadrado, I.; Losada, J. *Organometallics* **1993**, *12*, 811. (g) Curran, D. J.; Graham, P. B.; Rausch, M. D. *Organometallics* **1993**, *12*, 2380. (h) Hartl, F.; Luyten, H.; Nieuwenhuis, H. A.; Schoemaker, G. C. *Appl. Spectrosc.* **1994**, *48*, 1522. (i) Atwood, C. G.; Geiger, W. E.; Bitterwolf, T. E. *J. Electroanal. Chem.*, in press.

[3] (a) Hawkridge, F. M. In *Laboratory Techniques in Electroanalytical Chemistry;* Kissinger, P. T., Heineman, W. R., Eds., Marcel Dekker: New York, 1984; p 355. (b) Graham, P. B.; Curran, D. J. *Anal. Chem.* **1992**, *64*, 2688.

[4] (a) Reference 3a, pp 337 ff. (b) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980; p 375. (c) We employed the same three-compartment (working, auxiliary, reference) cell design used in our laboratory for bulk electrolyses.

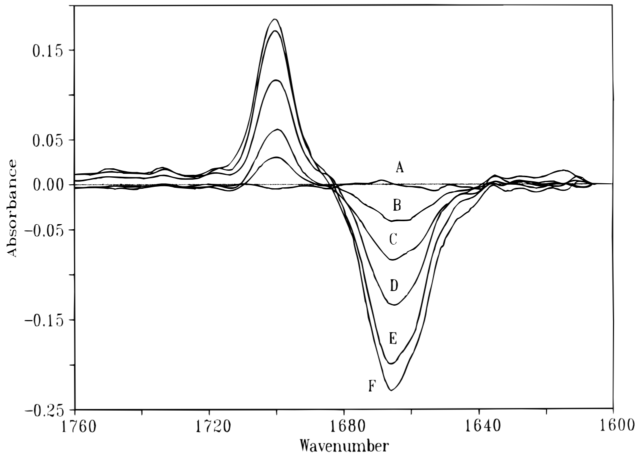


Figure 3. Difference spectra obtained during anodic electrolysis of 1.0 mM acetylferrocene (**2**) in CH_2Cl_2/0.1 M $[NBu_4][PF_6]$ at 273 K. An increasing amount of acetylferrocenium ion is produced in the sequence A–F.

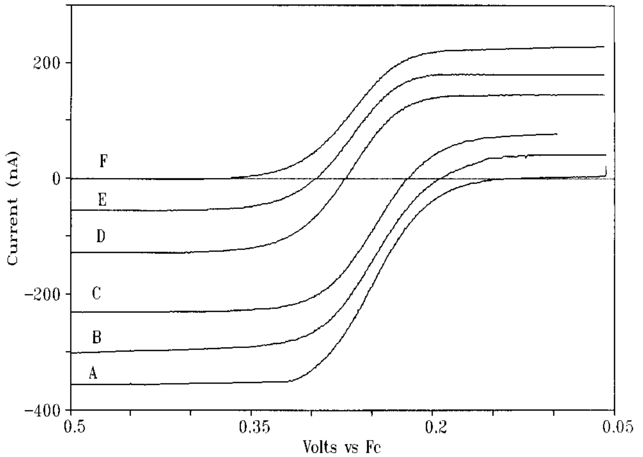


Figure 4. Representative steady-state voltammograms (scan rate 5 mV/s at a 250 μm Pt disk) of solutions A–F like those in Figure 3. The anodic current is negative. Scan A is that of 1.0 mM acetylferrocene and scan F that of nominally 1.0 mM acetylferrocenium ion.

mini- or microelectrodes were used for voltammetric scans. The IR cable is carried in a 7 mm (o.d.) stainless steel housing through an entry port in the top of the cell, analogous to how an electrode would be placed into the solution. The probe samples the the bulk solution rather than the electrode reaction layer.

A bifurcated 1 m fiber-optic chalcogenide cable[5] mounted on the exit port of a Mattson Polaris FTIR spectrometer carries the IR radiation[6] into the electrolysis cell and returns it to a HgCdTe detector. The probe terminates in a tip[5] into which the analyte solution is allowed to flow freely through entry holes (Figure 1). IR light enters the solution from the cable, bounces off a gold reflecting mirror on the end of an adjustable screw, and is returned to the detector by the cable. The optical path length (*b*) may be changed (*ca.* 1–5 mm) with the screw adjustment. The cable employed in this study has acceptable transmission in the spectral range 4000–860 cm^{-1}, except for an inaccessible segment at *ca.* 2220–2100 cm^{-1}. The ν_{CO}(asym) band at 1946 cm^{-1} for 0.89 mM $CpMn(CO)_3$ in hexane had a signal-to-background ratio >30 with $b = 1.2$ mm. Although the present experiments were carried out under argon using Schlenk procedures, the method should be easily adapted to drybox procedures and to vacuum or pressure cells.

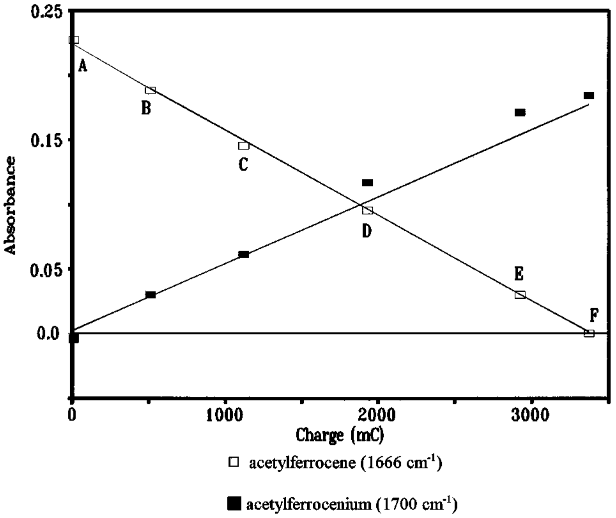
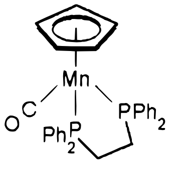


Figure 5. Absorbance changes observed in the experiment of Figure 3 plotted against the total amount of charge passed in the electrolysis. Passage of 1 faraday/mol required 3300 mC in this experiment.

Spectra prior to and after anodic electrolysis of CpMn(CO)(dppe) (**1**; dppe = 1,2-bis(diphenylphosphino)ethane) are shown in Figure 2. Neutral **1** (ν_{CO} 1826 cm^{-1}) was chosen for demonstration purposes because it is known to undergo one-electron oxidation ($E^{\circ\prime} = -0.05$ V *vs* Fc) to a persistent 17-electron monocation (ν_{CO} 1927 cm^{-1}).[7] Identical results were obtained between 298 and 235 K, demonstrating the applicability of this method to low-temperature studies.



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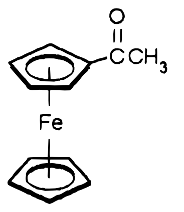

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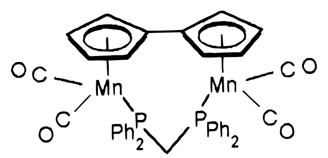

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The oxidation of 1.0 mM acetylferrocene (**2**, $E^{\circ\prime} = 0.27$ V *vs* ferrocene) was studied in CH_2Cl_2/0.1 M $[NBu_4][PF_6]$ at 273 K by monitoring the position and intensity of the organic carbonyl band as the electrolysis proceeded at $E_{appl} = 0.53$ V (ν_{CO} 1666 cm^{-1} for **2**; ν_{CO} 1700 cm^{-1} for $\mathbf{2}^+$), in this case as difference spectra (Figure 3). Progress of the conversion from **2** to $\mathbf{2}^+$ was also followed

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(5) Remspec Corp., Sturbridge, MA.

(6) The optical fiber bundle contains 7 input fibers and 12 output fibers within a stainless steel probe of *ca.* 8 mm diameter. An alternative to the transmission cell sample probe is one using a ZnSe crystal for attenuated total reflectance measurements.

(7) (a) Rehder, D.; Kececi, A. *Inorg. Chim. Acta* **1985**, *103*, 173. (b) Pike, R. D.; Rieger, A. L.; Rieger, P. H. *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 3913. (c) Connelly, N. G.; Freeman, M. J.; Orpen, A. G.; Sheehan, A. R.; Sheridan, J. B.; Sweigart, D. A. *J. Chem. Soc., Dalton Trans.* **1985**, 1019.

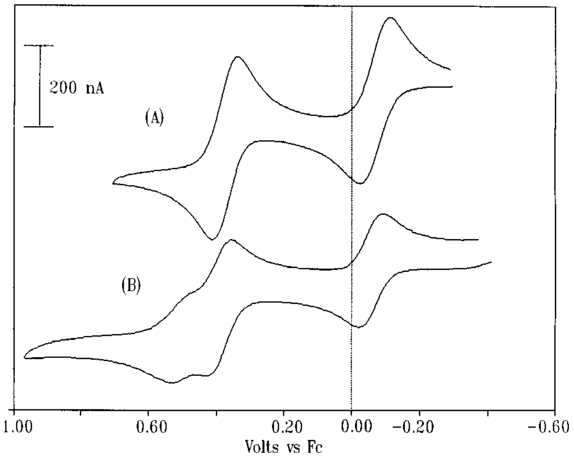

Figure 6. Cyclic voltammetry scans ($v = 0.2$ V/s) at a 250 μm Pt disk of (A) 1.0 mM (fulvalenyl)$Mn_2(CO)_4(\mu$-dppm) (**3**) in CH_2Cl_2/0.1 M $[NBu_4][PF_6]$ and (B) solution a after double oxidation ($E_{appl} = 0.8$ V) to $\mathbf{3}^{2+}$ followed by re-reduction at $E_{appl} = -0.4$ V. The new feature at *ca.* 0.5 V arises from a side product.

by voltammetry and coulometry. Slow linear scans at a small ($d = 250$ μm) Pt disk produced steady-state voltammograms allowing direct measurement of the relative amounts of **2** and $\mathbf{2}^+$ in solution from the ratios of anodic (for **2**) and cathodic (for $\mathbf{2}^+$) currents. The six voltammograms in Figure 4 correspond roughly to the six spectral samples in Figure 3. Moreover, the absorbances of the bands were directly proportional (1700 cm^{-1}, $\mathbf{2}^+$) or inversely proportional (1666 cm^{-1}, **2**) to the amount of charge passed in the electrolysis (Figure 5), thereby indicating that the mechanism of the oxidation does not change during the course of the electrolysis.

Evaluation of the electrochemical and spectral properties of electron-transfer side products was obtained in studies of the double oxidation of (fulvalenyl)$Mn_2(CO)_4(\mu$-dppm) (**3**; dppm = bis(diphenylphosphino)methane) (**3**). Complex **3** has two one-electron anodic processes that are chemically reversible in CV experiments ($E°_1{}' = -0.06$ V, $E°_2{}' = 0.40$ V).[8] After passage of 1 faraday of charge the solution had an IR spectrum identical with that reported earlier for $\mathbf{3}^+$.[8] The monocation was then electrolyzed to the dication $\mathbf{3}^{2+}$, after which the dication was reduced back to **3**. CV scans after the re-reduction (Figure 6) revealed the presence of another wave at *ca.* 0.5 V in addition to the two one-electron waves of **3**. Square-wave voltammetry confirmed the presence of a secondary compound. IR spectra after the back-and-forth electrolyses had two new features at 1950 and 1889 cm^{-1} (Figure 7). Taken together, the potential of the side product and the positions of its CO bands suggest a $CpMn(CO)_2L$ moiety, where L is a phosphine or related donor atom.

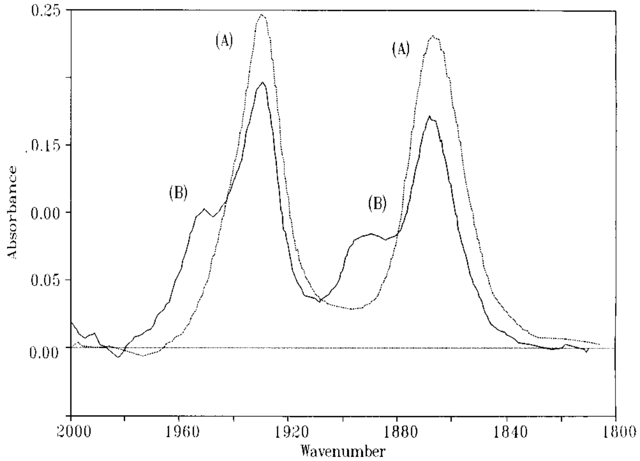

Figure 7. IR spectra in the 1800–2000 cm^{-1} range corresponding to solutions A and B of Figure 6.

The fiber-optic remote sensing technique provides high-quality spectra of electrolysis solutions over a sufficiently wide spectral range to be of interest to organometallic chemists working on a variety of redox problems. It is anticipated that the combination of *in situ* IR analysis and optimum electrochemical performance will lead to advances in quantitative organometallic electron-transfer studies, especially those involving closely spaced voltammetric waves or otherwise mechanistically complex reactions.

Acknowledgment. We gratefully acknowledge the financial support of the National Science Foundation (Grant No. CHE94-16611) and helpful conversations with Peter Melling.

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[8] Atwood, C. G.; Geiger, W. E.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 5310.