

## COMPACT FTIR SPECTROMETER INSIDE A GLOVEBOX: IR SPECTROELECTROCHEMISTRY AND OTHER APPLICATIONS

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We wish to report the advantages of using a compact FTIR spectrometer inside a glovebox to investigate air and moisture sensitive compounds. The FTIR spectrometer, manufactured by Midac Corporation<sup>1</sup>, measures only 18 cm x 28 cm x 61 cm and can be conveniently placed inside a standard Vacuum Atmospheres glovebox by way of the antechamber<sup>2,3</sup>. This match of a low cost, compact FTIR spectrometer with widely available glovebox technology affords researchers a simple, routine method for acquiring IR information for air and moisture sensitive compounds. Several applications are illustrated, with emphasis on the technique of IR spectroelectrochemistry. A simple design for an IR spectroelectrochemical cell is also described.

Standard glovebox and Schlenk techniques have made the manipulation of air and moisture sensitive compounds routine<sup>4</sup>. Air and/or moisture sensitive solutions are commonly prepared for IR analysis in an inert atmosphere using Schlenk techniques and then transferred to an IR cell using a syringe. Alternatively, a sample can be prepared and transferred to an IR cell inside a glovebox and then removed from the box for analysis. Nevertheless, these techniques may be undermined when employing standard, commercially available, demountable cells with Luer lock fittings. The reason for this is simple; most cells leak over time. In addition, the time delay (usually several minutes) between preparing the sample and obtaining a spectrum may preclude observation of unstable complexes. A solution to this problem is to place the entire FTIR spectrometer in an inert atmosphere. Until recently, this was not economically feasible because of the large footprint of most FTIR spectrometers. The Midac Corporation FTIR spectrometer has an unusually small footprint that allows it to be placed inside a glovebox with room to spare. The spectrometer is interfaced to a PC computer and is controlled using Spectra Calc software (Galactic Industries<sup>5</sup>).

One advantage that accrues from this set-up is the ease with which reactions can be monitored. Figure 1 illustrates an FTIR spectrum obtained less than 1 minute after addition of carbon dioxide to a solution of  $\text{Rh}(\text{PP}_3)\text{H}(\text{PP}_3 = \text{tris}(2\text{-(diphenylphosphino)ethyl)-phosphine})$  and sodium tetraphenylborate<sup>6</sup>. The IR spectrum shows three bands at 1720, 1360, and 1220 $\text{cm}^{-1}$  that are characteristic of a Rh-CO<sub>2</sub> intermediate<sup>7</sup>. Reaction kinetics (measured in a separate environment) establish that this intermediate is short-lived. It is generally difficult to observe reactive intermediates such as the Rh-CO<sub>2</sub> adduct using standard glovebox or Schlenk techniques and an external IR spectrometer. Within the time required to prepare the sample, transfer it to an external FTIR, and purge the sample chamber of atmospheric CO<sub>2</sub> and water vapor, reactive intermediates will likely decompose.

Reaction kinetics are also conveniently obtained using a Midac FTIR inside a glovebox<sup>8</sup>. We have obtained kinetic data for the reaction of 8-azidoquinoline with Mo(0) complex, Mo(CO)<sub>3</sub>(CH<sub>3</sub>CN)<sub>2</sub>(PPh<sub>3</sub>), by monitoring changes in infrared absorption bands over time<sup>9</sup>.

The disappearance of the azide band,  $\nu(\text{N}_3)$  at 2118 cm<sup>-1</sup> (Figure 2A), is concurrent with disappearance of the three carbonyl bands of Mo(CO)<sub>3</sub>(CH<sub>3</sub>CN)<sub>2</sub>(PPh<sub>3</sub>) (only the  $\nu(\text{C}=\text{O})$  stretch at 1925 cm<sup>-1</sup> is shown in the left hand portion of Figure 2B). Analysis of the kinetic data suggest that the reaction is first order in both Mo(CO)<sub>3</sub>(CH<sub>3</sub>CN)<sub>2</sub>(PPh<sub>3</sub>) and azide. Absorption bands due to the formation of a new carbonyl species (a phosphinimine complex, Mo(CO)<sub>4</sub>[N(PPh<sub>3</sub>)(C<sub>9</sub>H<sub>6</sub>N)]), can be seen growing in at 1890 cm<sup>-1</sup> (right hand side of Figure 2B) and at 2008 cm<sup>-1</sup> (Figure 2C). The experimental procedure was greatly simplified by monitoring the reaction inside the glovebox because the products are very air sensitive.

Spectroelectrochemistry is a technique that combines electrochemistry with a number of spectroscopic methods. These methods include examples from absorption (Mossbauer, X-ray, ellipsometry), scattering (X-ray fluorescence, photoemission, Raman fluorescence), resonance (NMR, ESR) and fragmentation (mass) spectroscopy<sup>10</sup>. FTIR spectroelectrochemistry is especially useful because it can provide detailed structural information about electrochemically generated species. Introduction of three electrodes into a solution IR cell exacerbates the problem of air and moisture leakage, making the cell design critical. Spectroelectrochemistry inside a glovebox circumvents the problem of contamination by air or moisture and therefore simplifies cell design. The spectroelectrochemical cell we have developed, illustrated in Figure 3, is based on a commercially available demountable FTIR cell<sup>11</sup>. The major modification is that the standard backplate has been replaced by a deeper one (easily constructed in a machine shop) to accommodate the thickness of a second needle plate. Both windows are drilled and separated by a 0.5mm Teflon spacer. The electrodes (Pt working, Pt auxiliary, and Ag reference) are introduced into the cell through three of the Luer lock openings of the needle plates and are passed through the drilled windows. Glass (or teflon) sleeves insulate the wires from the metal fittings. The fourth Luer lock fitting is used to introduce sample solution. Small rubber septa hold the electrodes in place where they exit the Luer lock fittings. Inside the IR cell (between the windows) the wires are carefully positioned so that there is no contact between electrodes. The Pt working electrode is threaded through a piece of Pt mesh centered in the window. The Pt mesh is essentially transparent to the IR beam allowing the cell to be used in the absorption mode. A low rate of diffusion is an important consideration when all three electrodes are in the same compartment<sup>12</sup>. The Pt mesh is advantageous in this regard in that diffusion is significantly reduced without producing an unreasonably high cell resistance. The solution is injected into the assembled cell through the unoccupied septum (a thin exit needle is placed in one of the other septa). Although this cell may be filled in a glovebox and used externally, we find that some leakage occurs over time, limiting the applicability of this cell for air sensitive reactions outside of an inert atmosphere.

The results of an FTIR spectroelectrochemical experiment are shown in Figure 4. A 10 mM solution of Cp<sup>\*</sup><sub>2</sub>Nb(Cl)(ketene)[Cp<sup>\*</sup>=C<sub>5</sub>H<sub>4</sub>Si(CH<sub>3</sub>)<sub>3</sub>; ketene=OCC(Ph)(Et)] in 0.8 M TBAH/THF [TBAH=tetra-N-butylammonium hexafluorophosphate] was reduced at -3.0 V (vs. Ag wire)<sup>13,14</sup>. By monitoring changes in the carbonyl region of the IR during electrolysis we observed the disappearance of the  $\nu(\text{C}=\text{O})$  stretch for the ketene ligand (at 1628 cm<sup>-1</sup>) and the appearance of a

broad band at  $1535\text{ cm}^{-1}$ , assigned as the one electron reduction product,  $[\text{Cp}'_2\text{Nb}(\text{Cl})(\text{ketene})]^-$ . When the cell is turned off,  $[\text{Cp}'_2\text{Nb}(\text{Cl})(\text{ketene})]^-$  reacts quickly via loss of chloride to produce a carbonyl complex with a band at  $1900\text{ cm}^{-1}$ . With our experimental setup, we were able to obtain high quality spectra in a reproducible fashion, as well as dramatically shorten the time between experiments for these highly air sensitive reactions.

The compact Midac FTIR placed inside a glovebox allows for routine sampling and characterization of air and moisture sensitive compounds. We have found that this setup makes IR spectroelectrochemical experiments especially convenient. The IR electrochemical cell, designed primarily from commercially available parts, is easy to assemble and makes the technique of spectroelectrochemistry more accessible to nonspecialists.

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## References

1. Midac Corporation, 1599 Superior Ave., Suite B3, Costa Mesa, CA, 92627.
2. Vacuum Atmospheres Company, 4652 Rosecrans Ave., Hawthorne, CA, 90250.
3. All compartment covers of the FTIR are removed before the instrument is placed into the antechamber to ensure complete removal of O<sub>2</sub>.
4. (a) D.F. Shriver and M.A. Drezdson, *The Manipulation of Air Sensitive Compounds*, John Wiley, New York, 1986. (b) A.L. Wayda and M.Y. Darensbourg (Eds.), *Experimental Organometallic Chemistry*, ACS Symposium Series #357, American Chemical Society, Washington, DC, 1987.
5. Galactic Industries Corporation, 395 Main Street, Salem, NH, 03079. The RS-232 cable required for instrument control was passed into the glovebox through a gas feed-through opening which was then sealed with caulking compound.
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8. Spectra Calc software facilitates the acquisition of repetitive spectral scans.
9. A. Saravanamuthu, J.-L. Fourquet, M. LeBlanc, M.R.M. Bruce, and A.E. Bruce, manuscript in progress.
10. R.J. Gale (Ed.), *Spectroelectrochemistry, Theory and Practice*, Plenum Press, New York, 1988.
11. The parts for the IR cell were purchased from Spectra-Tech, Inc., 6520 Glenbrook Rd., Stamford, CT, 06906.
12. Rapid diffusion of solution in a one compartment spectroelectrochemical cell is a problem because products generated at the auxiliary electrode may interfere with observation of products generated at the working electrode.

13. This research was done in collaboration with Professor Joseph W. Bruno, Wesleyan University, Middletown, CT. A. Saravanamuthu, A.E. Bruce, M.R.M. Bruce, M.C. Fermin, A.S. Hneihen, and J.W. Bruno, manuscript in progress.
14. In a typical reduction experiment the cell potential needed to be approximately 250 mV more negative than that employed in a standard electrochemical cell. This difference is undoubtedly due to cell resistance. Thus a -3.0 V, the solvent window still has not been reached.

### Figure Captions

Figure 1. FTIR spectrum of  $\text{Rh}(\text{PP}_3)\text{H}$  (0.1 mM) and  $\text{NaBPh}_4$  (0.2 mM) in THF obtained within the first 60 seconds of addition on  $\text{CO}_2$ .

Figure 2. Time dependent FTIR spectral changes in the reaction of 8-azidoquinoline (4.5 mM) and  $\text{Mo}(\text{CO})_3(\text{CH}_3\text{CN})_2(\text{PPh}_3)$  (4.5 mM). Numbers refer to time in seconds elapsed following mixing of reagents: (1) 146, (2) 178, (3) 239, (4) 299, (5) 359, (6) 419, (7) 479, (8) 539, (9) 599.

A. Disappearance of  $\nu(\text{N}_3)$  band at  $2118\text{cm}^{-1}$  for 8-azidoquinoline.

B. Disappearance of  $\nu(\text{C}=\text{O})$  band at  $1925\text{cm}^{-1}$  for  $\text{Mo}(\text{CO})_3(\text{CH}_3\text{CN})_2(\text{PPh}_3)$ , and appearance of  $\nu(\text{C}=\text{O})$  band at  $2008\text{cm}^{-1}$  for  $\text{Mo}(\text{CO})_4[\text{N}(\text{PPh}_3)(\text{C}_6\text{H}_6\text{N})]$ .

Figure 3. Schematic of FTIR spectroelectrochemistry cell.

Figure 4. FTIR spectral changes during spectroelectrochemical experiment of 10 mM  $\text{Cp}_2\text{Nb}(\text{Cl})(\text{ketene})$  in 0.8 M TBAH/THF: (1) before reduction, (2) after 8 min at -3.0 V (the cell was turned at  $t = 10$  min), (3)  $t = 14$  min, (4)  $t = 20$  min.