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STEP-SCAN FOURIER TRANSFORM INFRARED (FTIR) SPECTROMETER FOR
INVESTIGATING CHEMICAL REACTIONS OF ENERGY-RELATED MATERIALS

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Final Report Abstract

Two step-scan Fourier transform infrared (FTIR) spectrometers were purchased with URI-DOE funds by the University of Utah. These infrared spectrometers have been used to carry out the following investigations: the determination of strength of adsorption of organic molecules at the liquid-solid interface of coated attenuated total reflectance (ATR) elements, the kinetic study of the photoinitiated polymerization of a dental resin, the exploration of the kinetics of photochemical reactions of organic molecules in solution, and the development of a stopped-flow FTIR interface for measuring rates and mechanisms of reactions in solution that are not photoinitiated and do not have convenient ultraviolet-visible spectral features.

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A vacuum-bench, step-scan Fourier transform infrared (FTIR) spectrometer (IFS 66v/S) with an infrared microscope attachment was purchased with URI grant funds for the joint use of the research groups of Professors E.M. Eyring (Chemistry), J.M. Harris (Chemistry) and J.D. Miller (Metallurgical Engineering) at the University of Utah. The infrared microscope was subsequently (1997) traded in to the manufacturer (Bruker) with additional non-federal funds for a purge-bench, step-scan FTIR spectrometer (IFS 66/S). These two FTIR spectrometers have so far played the central role in the DOE funded research studies described below.

The vacuum bench FTIR in the J.M. Harris research laboratory has found several important applications. Harris and Dr. Peter E. Poston¹ have employed the instrument to study the mechanisms of adsorption at the liquid solid interface of ethylacetate to fumed silica deposited onto a ZnSe attenuated total internal reflectance (ATR) substrate. Using least square techniques, two adsorbates and a free solution species were resolved from the data. Surface sites responsible for the stronger adsorption interaction were found to be the vicinal silanol groups. Free energies of adsorption for the two species were estimated to be -4.7 and -3.3 kcal/mol from a simple Langmuir fit to the data, and equilibrium constants of 412 M^{-1} and 36 M^{-1} were also obtained. Harris and Dion Rivera, a graduate student, are presently extending this work to sol-gel coated Ge ATR elements. These elements have been derivatized with 3-aminopropyltriethoxysilane and present studies are concentrating on quantitatively characterizing the derivatized surface using the FTIR. The long term goal of this research is to elucidate the kinetics of

photobinding, with molecules like benzophenone, to these derivatized surfaces using the rapid scan capabilities of the FTIR.

Rapid scan is also being used by Harris, Poston, and Rivera to study the kinetics of photoinitiated polymer curing reactions on the time scale of several seconds using a diffuse reflectance apparatus. The photoinitiated polymerization of a dental resin is a now familiar application of this chemistry. Research is still in the preliminary stages, but initial results show clean infrared spectra of photoinitiated curing in polymer films easily obtainable on this time scale with the FTIR spectrometer operated in the rapid scan mode.

So far, the main use of the vacuum bench FTIR has been the application of its step-scan capabilities to the study of the kinetics and mechanism of photochemical reactions of organic compounds in the solution phase taking place on the microsecond time scale. These studies have proven to be very challenging due to the heating of the sample caused by the incident laser pulse. This heating launches acoustic waves and causes index of refraction gradients to appear in the liquid sample volume.² These events modulate the IR beam and appear as a modulated event in the step-scan mode making it very difficult to separate the thermal signal from the photochemical signal. Initial work with factor analysis showed some promise in separating the signals, but repeatability was a serious problem. Another problem is the small change in bond order that occurs in the photoexcitation of organic compounds compared to the organometallic³⁻⁶ or biological⁷⁻⁹ systems that have been previously studied with this technique. This smaller change in bond order causes a smaller modulation making the signal from the transient species harder to

detect. Currently, Harris and Rivera are employing a Nd:YLF laser with a high repetition rate (1000 Hz) to allow a large number of spectra to be acquired quickly and thus maximize the signal to noise ratio. IR filters are also being employed to eliminate thermal modulations caused by strongly absorbing solvent bands. These modifications to the step-scan experiment should allow signals from photochemical processes to be studied more easily with the FTIR.

The purge bench FTIR installed in E.M. Eyring's research lab first met the manufacturer's specifications in January, 1997. It has since been used primarily by Brian Dunn (Ph.D. from Wayne State University, 1996) to carry out the experiments described below.

Since many of the reactions studied by the Eyring group are not photoinitiated, it was necessary that a rapid-mixing stopped-flow device be constructed capable of interfacing to the FTIR spectrometer. Dr. Dunn built the device in the typical five syringe-three valve configuration common to stopped-flow instrumentation. All components were commercially available, so fabrication of custom parts was unnecessary. In this FTIR application, the time limiting factor is the time required to collect an interferogram and not the mixing time of the stopped-flow attachment. Thus it was unnecessary for the attachment to achieve sample mixing in a very short time (<100 msec).

The construction of the stopped-flow attachment was accomplished with five Hamilton 10 mL Gastight syringes (Hamilton Part #81620), three Hamilton 3-port valves (Hamilton Part #86777), one Hamilton 3-way "Y" junction (Hamilton Part #32814), 18 gauge Teflon tubing (Hamilton Part #88907), various fittings for the tubing connections, and a

SpectraTech NaCl sealed flow infrared cell (SpectraTech Part #FT54-755). A drawing of the unit is shown in Figure 1.

The triggering of the FTIR spectrometer to initiate data acquisition after the flow has stopped is of critical importance. The spectrometer accepts a trigger signal via a TTL I/O port. However, the OPUS software provided by the manufacturer does not support this function. The software will begin data acquisition when a key is pressed on the connected computer, so the computer keyboard was modified to accept a trigger signal from the stopped-flow unit. The diagram of the electronic circuit constructed by Dr. Dunn for this purpose is shown in Figure 2.

The initial experiment using the stopped-flow attachment interfaced to the FTIR spectrometer was a reinvestigation¹⁰ of the kinetics of the substitution reaction between the bidentate ligand 1,10-phenanthroline and pentacarbonyl tungsten, $\text{W}(\text{CO})_5(\text{THF})$. The $\text{W}(\text{CO})_5(\text{THF})$ species was generated in solution by photolysis of $\text{W}(\text{CO})_6$ in THF using a xenon arc lamp. The reaction was monitored in the FTIR spectrometer by acquiring time-resolved infrared spectra. The reaction showed the expected decrease in absorbance (see Figure 3) at $\sim 1930\text{ cm}^{-1}$ which is due to the reaction of $\text{W}(\text{CO})_5(\text{THF})$ with 1,10-phenanthroline. In addition, this system showed some unexpected behavior (see Figure 4) after the substitution reaction was completed. A relatively large peak in the absorbance spectra started to appear about four seconds after the reactants were mixed. This peak is most likely due to decomposition of the $\text{W}(\text{CO})_5(\text{THF})$ brought about by dissolved oxygen in the phenanthroline solution. This peak would have gone undetected in a conventional stopped-

flow experiment where only one wavelength of infrared light is used to monitor the reaction. A manuscript describing these stopped-flow FTIR experiments that will acknowledge URI funding of the spectrometer is in preparation.¹¹

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Figure 1. Diagram of Stopped-Flow Attachment

Figure 2. Diagram of Triggering Circuit.

Figure 3. Change in Absorbance due to $\text{W(CO)}_5(\text{THF})$.

Figure 4. Time Resolved Spectra of Reaction Mixture of $\text{W(CO)}_5(\text{THF})$ and Phenanthroline