APPLICATION NOTE

FT-IR Spectroscopy

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Monitoring Fast Chemical Reactions using Stopped-flow on a Rapid Scanning FT-IR Spectrometer

Introduction

It is important to understand what is happening during chemical reactions in order to optimize the chemical process, determine reaction times, and completion. Some chemical reactions can occur extremely fast and can consist of multiple steps. In order to understand the chemistry occurring, it is essential to use an analytical technique that can identify and monitor the concentrations of chemical species present at any time during the reaction. Spectroscopic techniques, especially infrared (IR) spectroscopy, can give specific chemical information, identifying intermediates and products during a reaction based on the spectral information collected. Modern FT-IR (fourier transform infrared) spectrometers, such as the PerkinElmer Spectrum 3™ FT-IR (Figure 1), have fast scan capabilities allowing for fast chemical reactions to be monitored in real time.

One of the most frequently used rapid kinetics techniques is **stopped-flow**. Small volumes of solutions are rapidly driven from syringes into a high efficiency mixer to initiate a fast reaction. It is commonplace to monitor such reactions using UV-Visible absorbance or fluorescence. These techniques are useful for monitoring reaction progress. In some cases, such monitoring may not produce useful information about the chemistry of the reaction if it cannot identify the species present. However, the coupling of an FT-IR spectrometer with a stopped flow system can generate significant spectral and chemical information whilst retaining the integrity of the fast chemical reaction.

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Figure 1. The PerkinElmer Spectrum 3 FT-IR.

Stopped-flow Experiments on the Spectrum 3 FT-IR Spectrometer

The stopped-flow system SF-73/FT-IR (Figure 2), from TgK Scientific Limited, Bradford-on-Avon, UK, was connected into the standard transmission slide mount in the sample compartment of the Spectrum 3. The reaction chamber consists of an integrated mixing cell in a 100 microns pathlength calcium fluoride transmission cell. The schematic of the stopped-flow system is shown in Figure 3.

The reactant solutions are placed in separate syringes in the stopped-flow accessory. Small volumes of these solutions are then rapidly driven from these syringes into a high efficiency mixer to initiate a fast reaction. The resultant reaction volume then displaces the contents of the optical cell filling it with freshly mixed reacting reagents. The volume injected is limited by the movement of the motor driven push plate and hence, the "stopped-flow". Throughout this process, the FT-IR spectrometer will be scanning the spectral data in a continuous time-resolved manner.

The Spectrum 3 FT-IR spectrometer can be run in a "fast-scan" mode using Spectrum™ Timebase software allowing for rapid spectral data collection, with scan rates in the order of 100 spectra per second enabling sub second reactions to be easily monitored. The data collection on the FT-IR can be synchronized with the stopped-flow injection using triggering mechanisms from the stopped-flow system.

The Ester Hydrolysis of Methyl Chloroacetate (MCA)

Esters will undergo hydrolysis to produce a carboxylic acid and an alcohol. The mechanism of the hydrolysis will depend on whether the reaction takes place in an acidic or basic solution. These reactions can be monitored using the stopped-flow FT-IR system. The stopped-flow syringes 1 and 2 were filled with:

(1) MCA adjusted to 10 mM with D_2O.

(2) an excess concentration (100 mM) of NaOH prepared in D_2O.

The experiment was performed at a 20 °C room temperature.

Figure 2. Stopped-flow system SF-73/FT-IR from TgK Scientific Limited.

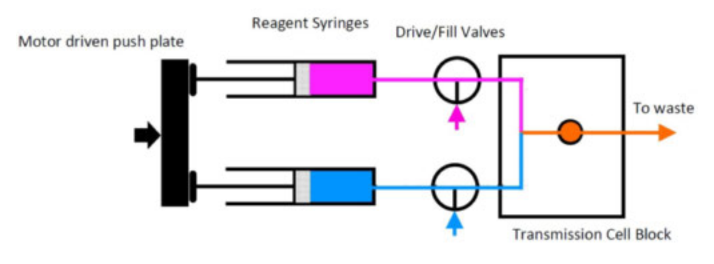

Figure 3. Schematic of the stopped-flow system.

FT-IR spectra were collected using a range of different resolutions and scan speeds over a series of experiments. The background was collected with pure D_2O in the cell.

In order to collect at the fastest scan rates, the instrument was set to run at 12 cm sec^{-1} OPD (optical path difference) velocity and 64 cm^{-1} spectral resolution. Data was collected over a period of 10 seconds at a rate of 101 spectra per second. The raw absorbance data is shown as Figure 4.

It can be clearly seen that there are significant changes in the spectral peaks at 1732 cm^{-1}, 1594 cm^{-1} and approximately 1310 cm^{-1}.

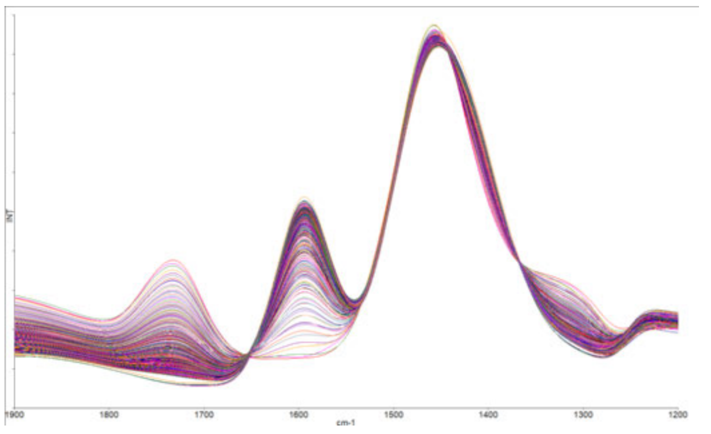

Figure 4. Spectral data from hydrolysis of MCA at 64 cm^{-1} resolution.

The same experiment was repeated at 16 cm^{-1} resolution, generating the raw absorbance spectra shown in Figure 5 at a rate of nearly 50 spectra per second.

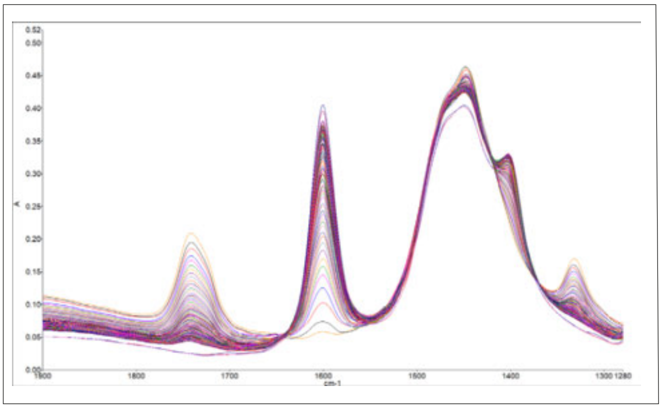

Figure 5. Spectral data from hydrolysis of MCA at 16 cm^{-1} resolution.

There is clearly a higher resolution of the spectral peaks at this resolution, sufficient for this experiment. In order to highlight the spectral changes, it is possible to generate differential spectra by subtracting the first spectrum of the series from all subsequent spectra as shown in Figure 6. This leads to a series of positive and negative peaks as the concentrations of the individual components increase and decrease respectively.

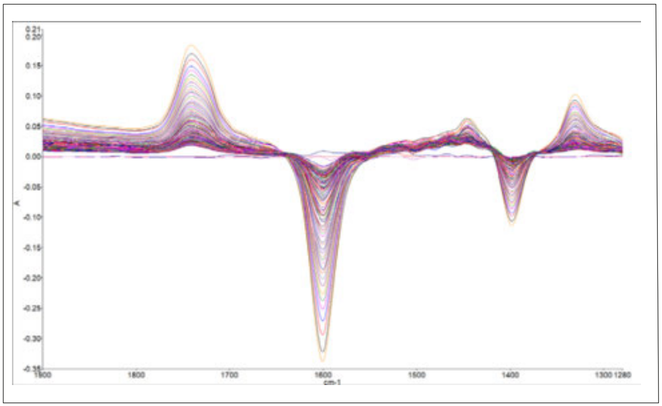

Figure 6. Differential spectra from the 16 cm^{-1} experiment.

From this plot it is clear that there are four spectral bands with major changes and a fifth band around 1445 cm^{-1} with minor changes. Intensity profiles for each of the spectral bands can be generated to trace the intensity of a peak versus time during the experiment. Profiles were generated for each of the four major band changes as shown in Figure 7.

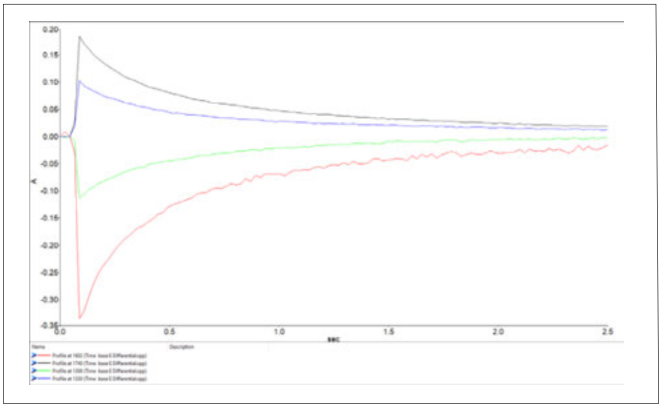

Figure 7. Intensity profiles at 1740 cm^{-1}(black), 1602 cm^{-1} (red), 1398 cm^{-1} (green), 1330 cm^{-1}(blue).

The intensity profiles show clear changes during the experiment and indicate when the reaction is complete, as the intensities no longer change. At these instrument settings the rapid onset of the reaction is easily tracked with a sufficient rate of spectral generation.

Summary

The PerkinElmer Spectrum 3 equipped with the stopped-flow system SF-73/FT-IR from TgK Scientific provides valuable information on rapid kinetic experiments. This experiment is perfectly suited to the rapid scan rates available on the Spectrum 3 and the transmission cell gives sufficient variation in the spectral bands. For cases where the spectral bands are relatively stronger, an ATR (attenuated total reflectance) version of the stopped-flow accessory - SF-73/ATR is available that works with the Specac Golden Gate ATR on the Spectrum 3.

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