REMSPEC **Application Note**

#00-03 In-Situ Monitoring of a Ketene Formation Reaction

Introduction

The formation of ketene intermediates is a crucial step in the synthesis of some important classes of compounds, including β-lactones. In the laboratory, this reaction is typically carried out at low temperature, to facilitate accumulation of the highly reactive ketene species before addition of reagents for the next reaction step. Monitoring the formation of the ketene is a challenge; removal of analytical samples from the reactor invites degradation of the ketene before it is characterized, and can compromise the reaction conditions. A sensitive in-situ method is needed, and fiber optic FTIR spectroscopy lens itself well to this task.

Real-Time In-Situ Monitoring

Real-time, in-situ monitoring of reaction progress is the ideal answer to questions about reactions that involve highly reactive intermediates. When the reactants, products or intermediates are infrared active, the integrated Remspec ReactionView™ System provides the answer. With this system, any liquid-phase reaction can be monitored, even when a solid catalyst is present. When reactant concentrations are lower than about 0.5%, and when solvents with low infrared absorbance are used, the ReactionView™ system uses a liquid transmission head (see Figure 1). The path length of this "double-pass" cell is adjustable from a few tenths of a millimeter to about 6 millimeters. Room temperature and refluxing reactions, and reactions well below room temperature, can readily be monitored using the Remspec probe, allowing the chemist to know the status of a reaction in real-time. The evolution and consumption of intermediate species can be viewed and correlated with the overall behavior, yield, etc. of the reaction. An added advantage is the slim design of the Remspec probe which allows it to be used with standard laboratory glassware – no special fittings are needed. The overall result is enhanced understanding of reactions and reaction mechanisms, leading to improved yields, higher-purity end products, and better control over side reactions.

Figure 1: The liquid transmission head of a Remspec Mid-IR Fiber Optic Immersion Probe; the diameter of the head – and the probe shaft – is about 6 mm.

Experimental:

Preparation of ketene from acetyl chloride:

$$CH_3COCl \xrightarrow{\text{eliminate HCl}} CH_2{=}C{=}O$$

This experiment was performed using a Remspec ReactionView™ system fitted with a low temperature extension and a liquid transmission head. The reaction was carried out at approx. -25°C in a three-necked reaction tube equipped with a magnetic stir bar and purged with nitrogen. The probe was inserted through a standard thermometer fitting to fully immerse the head.

Reagents:

methylene chloride, 8.0 ml
Hunig's base, 0.05 mmoles
acetyl chloride, 0.25 mmol in 2.0 ml methylene chloride

The methylene chloride was charged into the magnetically stirred flask, which was purged with nitrogen, and a background spectrum was obtained. The Hunig's base was added and automatic data collection was begun (one spectrum every minute), then addition of the acetyl chloride was begun in increments of approx. 0.1 µl every 30 minutes.

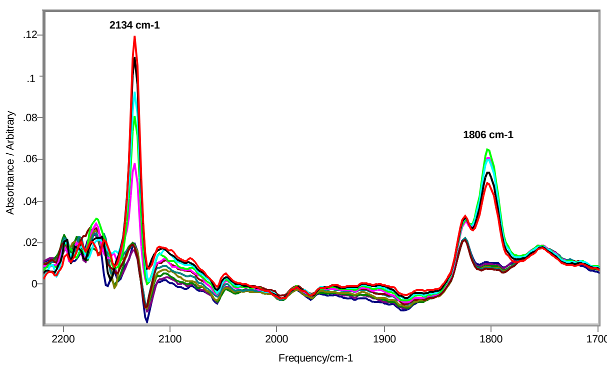

Figure 2: Mid-IR spectra of reaction mixture at 1 min. intervals from 39 to 50 min

Discussion

Figure 2 shows selected spectra obtained just before, during, and after the addition of one increment of the acetyl chloride. Two peaks were monitored: the ketene C=C=O stretch at 2134 cm^{-1} and the acetyl chloride C=O stretch at 1806 cm^{-1}. The heavy red trace represents the final spectrum in the group; clearly the ketene peak is growing as the acetyl chloride peak diminishes.

Figure 3 is a plot of the peak areas for the ketene and acetyl chloride peaks versus time for the first hour of the reaction. The graph clearly shows that the acetyl chloride peak increases sharply as the reagent is added, then diminishes as it is consumed. The peak at 2134 cm^{-1} due to the product ketene develops after the addition of the acetyl chloride, lagging by a time of no more than one minute. After formation, the ketene slowly disappears; this may be due to the presence of moisture traces, or improper temperature control.

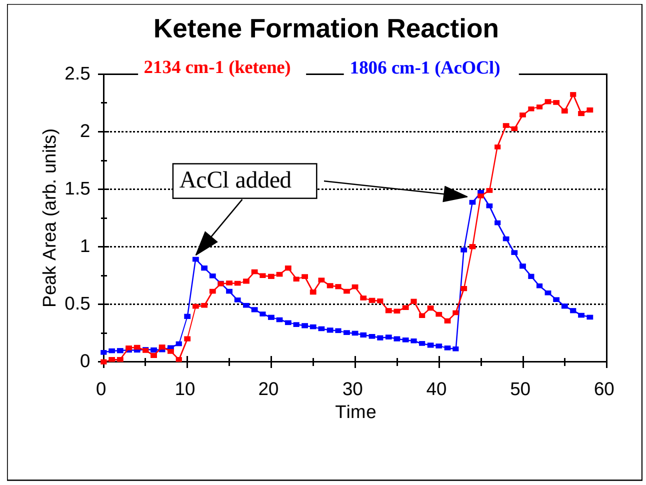

Figure 3: Graph of peak area versus time at 2134 cm^{-1} and 1806 cm^{-1} during ketene formation reaction.

Commentary

This reaction is typical of synthetic steps that are performed in laboratories every day. By selecting strong, isolated ketene and carbonyl stretches in the product and regent spectra as the peaks to be monitored, it was easy to plot the concentration/time graph for the appearance of ketene and the consumption of acetyl chloride even at concentrations as low as 100 ppm. For routine use, or for industrial process monitoring, automatic, real-time display of concentration/time curves for reactants, intermediates, or products can be programmed using the spectrometer control software.

The use of the Remspec ReactionView™ gives the scientist or engineer the ability to follow the course of any reaction, organic or inorganic, rapid or slow, and in any liquid medium desired -- aqueous or non-aqueous -- for improved analytical and synthetic productivity.

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