

Kinetic and Mechanistic Studies on the Heck Reaction using On-line Spectroscopy



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Introduction

Catalytic reactions are usually monitored by gas chromatography (GC), liquid chromatography (LC) or mass spectrometry (MS). These are invasive, often time consuming and may require sample handling (filtration, extraction, dilution). Vibrational spectroscopic techniques, like Fourier transform near infrared (FT-NIR) and Raman, are fast, non-invasive and require no sample handling. Furthermore, information regarding the chemical composition can efficiently be obtained from the spectral data. Therefore, such techniques are ideally suited for real time monitoring of chemical reactions.

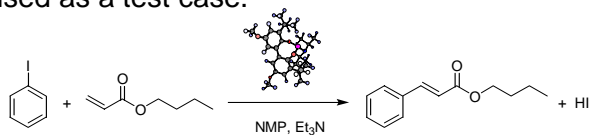
Two problems associated with spectroscopy as a tool for chemical analysis:

- Large amounts of data are generated;
- Calibration is time consuming and complex.

We develop chemometric tools to lower the calibration effort associated with spectroscopy and to estimate kinetic parameters from large sets of spectroscopic data.

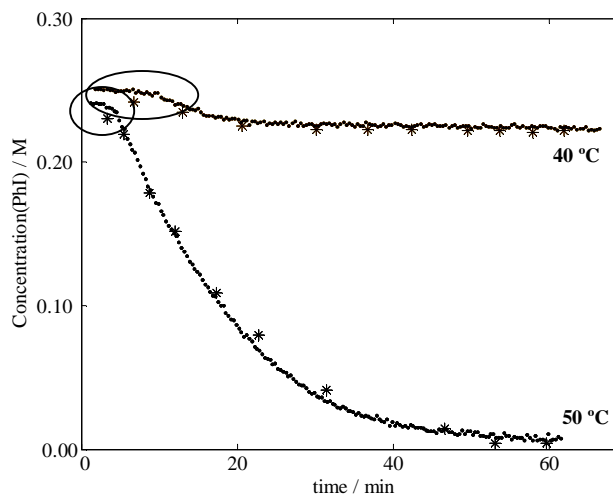
Results

The fast Heck coupling between Iodobenzene (PhI) and *n*-butyl acrylate (NBA) in *n*-methyl pyrrolidinone (NMP), catalyzed by a bulky monodentate phosphoramidite catalyst was used as a test case.



This complex reaction in liquid phase was monitored in real time by FT-NIR spectroscopy, using GC as a reference method. Each reaction was performed in batch mode at 40 and 50 °C. Spectral data was

analysed using the Net Analyte Signal (NAS) approach, and GC data calibration was carried out by linear regression performed on data relative to internal standard.



The profiles obtained from GC and FT-NIR are consistent. At 50 °C, the initiation period is barely visible in the GC data, but still well observable using NIR spectroscopy. This period may reflect the catalyst dimer-monomer equilibrium. Further studies are in progress. This work has been submitted for publication [1].

Conclusions

The feasibility of monitoring the Heck reaction by in-situ NIR spectroscopy has been demonstrated. The advantages of fast spectroscopy are clear, as it gives more information about the reaction over the same period of time.

[1] S. C. Cruz, P. J. Aarnoutse, G. Rothenberg, J. A. Westerhuis, A.K. Smilde and A. Blik, 2003, submitted.