POC4SOC

Session 4: Techniques for Data Collection

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Session Overview

- Types of data
- Overview of analysis requirements
- Errors
- Techniques
  - Availability
  - Sensitivity
  - Time-scale
  - Benefits
  - Pitfalls and drawbacks

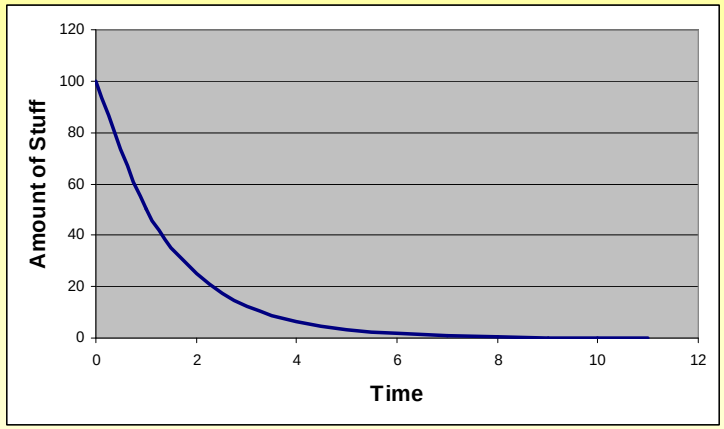
Data Collection

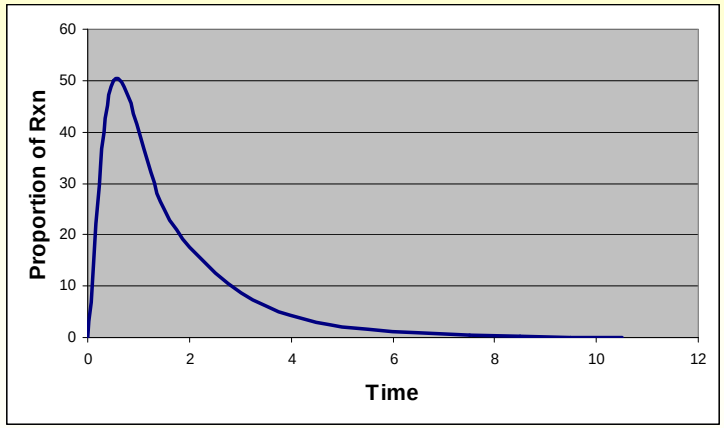
- If you remember only one thing from this session please make it:

“Get good quality data!”

- Poor quality data will make interpretation.
  - Difficult at best
  - Impossible at worst
- Any technique that can be related to concentration and followed as a function of time can be used.

Types of Data





- Most common type of graph [Stuff] vs time eg HPLC, NMR, IR, etc.
- On-line and off-line analysis.
- **Differentiate** to obtain rate at any point in time!

- Less common but useful eg heat flow.
- **Integrate** to obtain rate at any point in time!

Types of Data

- Further divided into:

1. On-line analysis.
2. Off-line analysis.

On-line Analysis

- Very powerful approach.
- Allow analysis of reaction in real time.
- Typically spectroscopic.
  - UV/vis, IR, polarimetry, NMR.
  - Highly useful for (Pseudo) 1st Order Kinetics as absorption is proportional to concentration *via* Beer's law.

Off-line Analysis Desirables

- Typically more difficult to relate to solution concentrations.
- Quantitative analysis (of isothermal reaction).
- Samples must be quenched for off-line analysis.
- Samples must be stable.
- We need molar response factors – standards, calibrations, Internal Standards.

Off-line Errors

- Errors can occur in any analysis.
- We need to be aware of how they can occur and what the impact might be.
- Sample amount.
- Diluent amount.
- Injection volume.
- Non-linear response in detector.
- Integration errors.

HPLC, GC

Availability – Good

Sensitivity – Excellent; will cover major components accurately

Time-scale – Poor, requires off-line analysis and sample quenching

Benefits – Lots of data, including minor components

Drawbacks – Requires analytical investment prior to experimentation

Chromatography Output

- Either a series of plots or a table of data.
- Data tends to be response *vs* time.
- Not always easy to convert to concentration data (more next session).
- Can be laborious to manipulate large amounts of data.

NMR

Availability - Good

Sensitivity – Moderate ± 2%

Time-scale – Minutes to hours

Benefits – Can monitor actual reaction rather than just samples. Multiple nuclei available. Easy to convert to concentration data.

Drawbacks – You do need to have clear resolution and homogeneous reactions.

NMR – Problem Reaction

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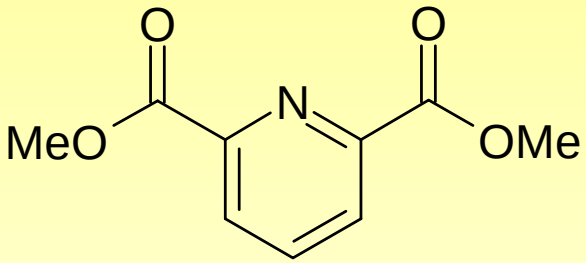
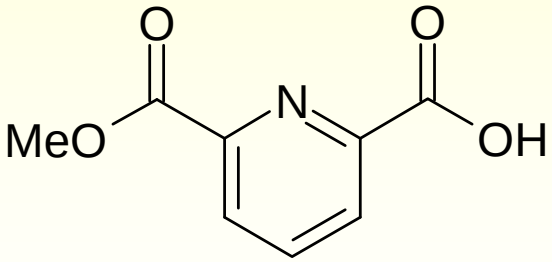
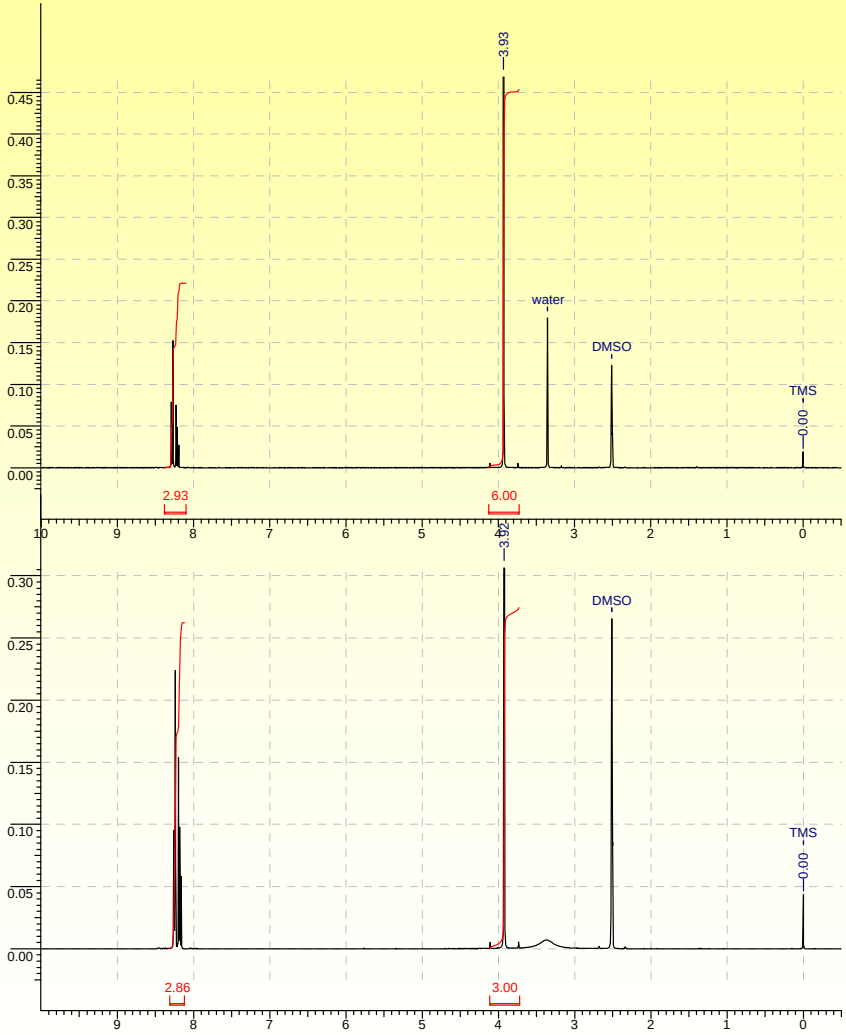


KOH;
HCl





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NMR – Easier Reaction

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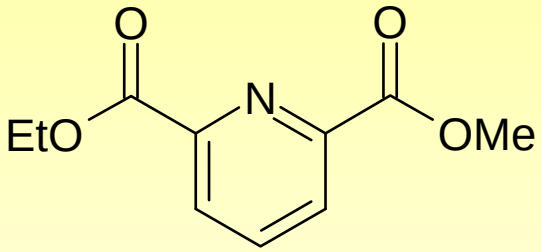

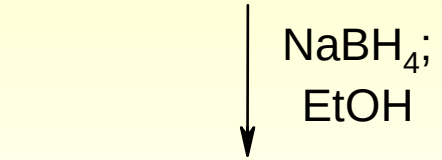

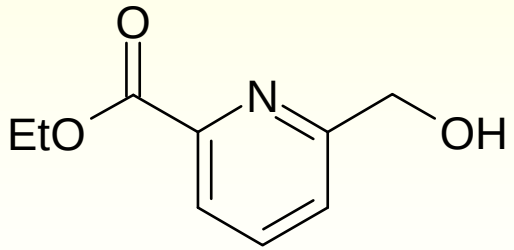

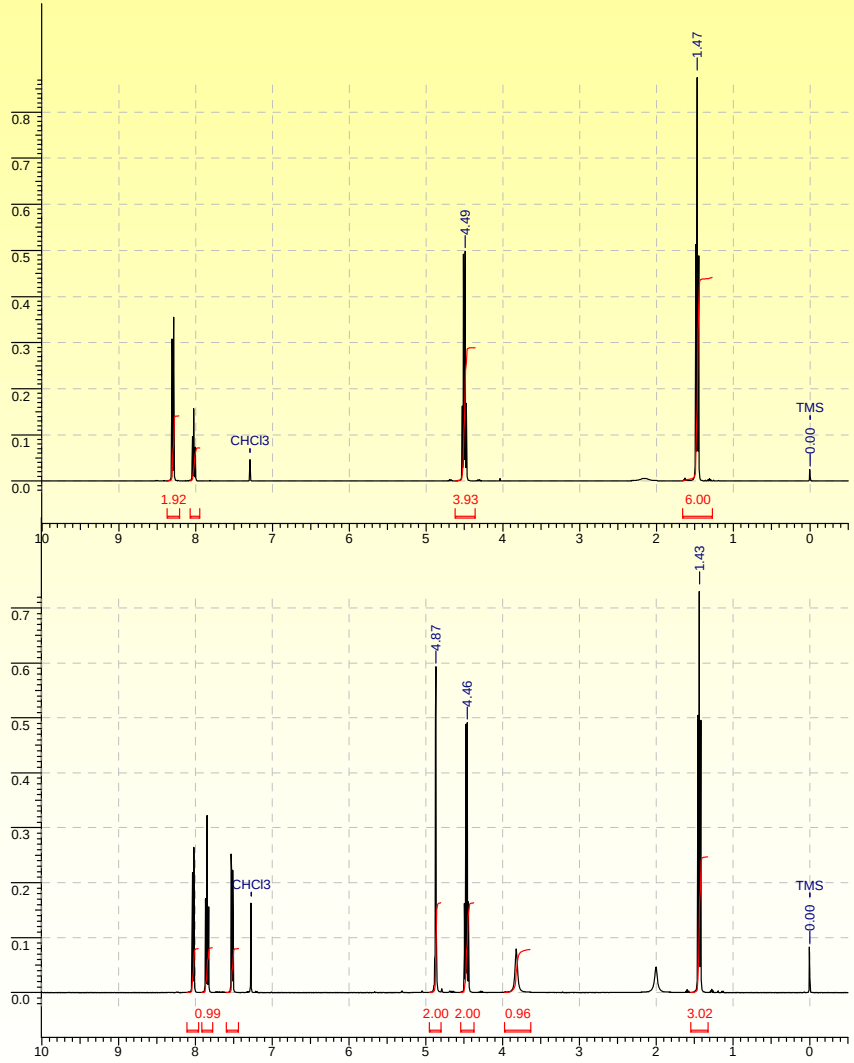

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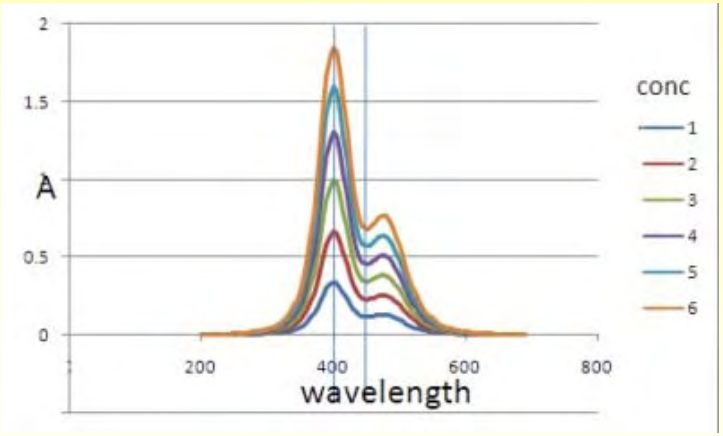
UV, IR

- Availability – Moderate
- Sensitivity – Moderate; will cover major components accurately
- Time-scale – <1 sec (UV) to >4 sec (IR)
- Benefits – Allows in situ analysis of reactive intermediates. Concentration proportional to absorption
- Drawbacks – Reaction MUST be homogeneous and transparent

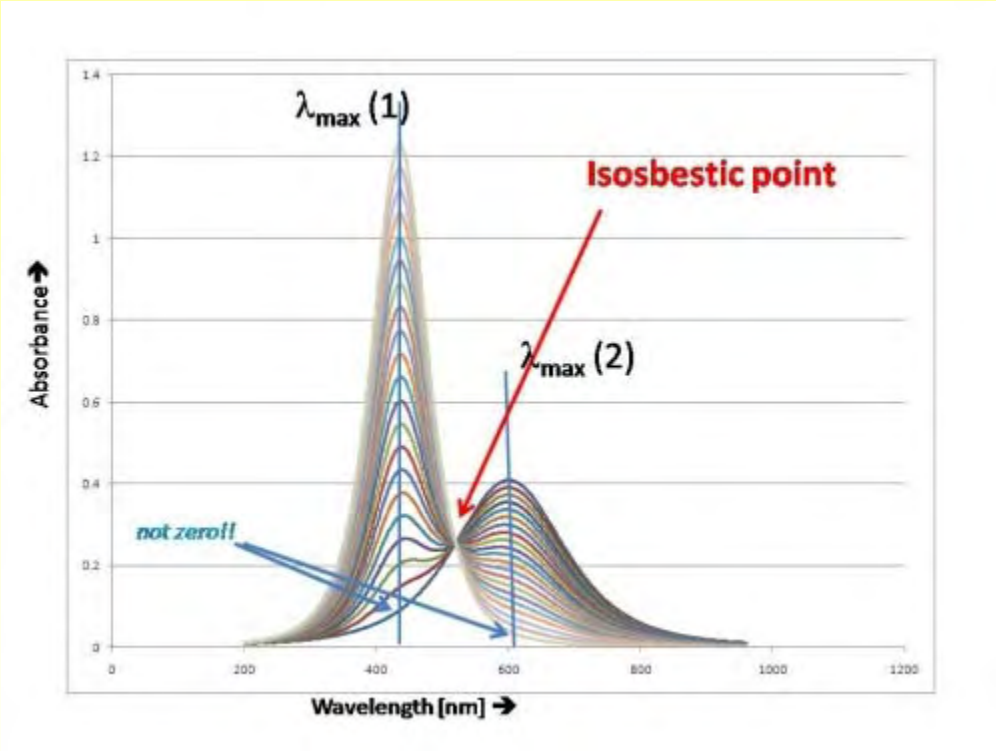
UV/Vis Output

- Typically a series of overlay plots.
- Easy to calibrate for pure species but for two reacting species overlap causes non-zero absorption despite zero concentration.



Isosbestic Point - Significance

- The isosbestic point is the wavelength where the total absorption does not change during the course of the reaction ie. $\varepsilon_{subst} = \varepsilon_{prod}$
- A good indication that long-lived intermediates are not present.
- If it moves or is out of focus, indicates extra complexity.



ReactIR Output

- Allows use of algorithms to pull out trends.
- Allows second derivative analysis to detect changes.
- Some software allows trending of peaks of unknown bond excitation.
  - ReactIR will show **all** species including by-products.

TLC

Availability – Excellent

Sensitivity – Moderate; requires work

Time-scale – Reaction of minutes

Benefits – Cheap, allows easy calibration of response to concentration

Drawbacks – High calibration effort.

Polarimetry

Availability – Reasonable

Sensitivity – Poor

Time-scale – Rapid

Benefits – Good for racemisation

Drawbacks – Only good for racemisation!

pH Changes

Availability – Excellent

Sensitivity – Poor, logarithmic scale

Time-scale – Rapid

Benefits – Cheap and quick

Drawbacks – Crude response

Fast Kinetics Techniques

- If $t_{1/2}$ is very short (i.e. < a few seconds) the above techniques display limitations.
- Can turn to:
  - Flow techniques i.e Stopped-flow method
  - Flash photolysis
  - Pulse radiolysis for radical chemistry
- See your specialist collaborator!

Summary

- The answer to “What can I use?” is often “What have you got and what’s your chemistry?”
- You can use anything that you can relate to concentration.
  - Be inventive!