Using $^1$H NMR to Monitor 1st-Order Kinetics

- Recall what for a process...

  $A \rightarrow B$

- We may write that

  $\frac{d[A]}{dt} = k[A] \Rightarrow \frac{d[A]}{[A]} = -kt$

- Integration leads to:

  $\ln[A] = -kt + \ln[A]_0$

  $\ln[A] - \ln[A]_0 = -kt$

  $\ln \frac{[A]}{[A]_0} = -kt$

  $\frac{[A]}{[A]_0} = e^{-kt}$

  $[A] = [A]_0 e^{-kt}$
To monitor [A] using NMR, we need to record spectra at (regular) time intervals...

Arrays!

Virtually any variable in NMR can be arrayed.

We can evaluate [A] if we can

1) Identify a resonance in molecule A that decreases in intensity as [A] decreases

2) Record identical NMR spectra over time

There are at least two ways to array acquisition parameters:

```
pw = 1, 2, 3, 4, 5, ...
array('pw', 40, 1, 1)  \rightarrow\ pw = 1, 2, 3, 4, 5, ...
```

Note: increasing
• The first approach, explicit, supports arbitrary order:

\[ pw = 1, 2, 4, 6, 8, \ldots \]
\[ pw = 1, 1, 2, 3, 4, 60, 3, \ldots \]

• The second approach, implicit, is easier for "regular" arrays

\[ \text{array}(\{'pw', 40, 1, 1\}) \] Implies pw array of 1 \( \Rightarrow 40 \) by 1 and increasing

\[ \text{array}(\{'pw', 20, 2, 2\}) \] Implies pw array of 2 \( \Rightarrow 40 \) by 2 and increasing

\[ \text{array}(\{'value', # in array, first, increment\}) \]
- So, for a kinetic series, what do we array?

- In addition to the explicit parameters identified by dps, there is a "hidden", pre-acquisition delay (pad) variable.

- pad is usually set to zero (seconds)

- pad only acts before the first transient
• pad can controlled the time between H
  7D spectra

• For kinetics, we want pad to be a constant
  value, e.g. 60 seconds, 1800 seconds, etc

• Explicit example - 60 seconds between the
  end of one experiment and the beginning
  of the next:

    pad = 0, 60, 60, 60, 60, ...

    ... but painful!

• Implicit example:

    arrag('pad', 40, 60, 0) = 60, 60, 60, 60, ...

    Note: initial value = 60
    increment = 0
• Implicit can't
  Now to force the first element
to 0, you must adjust the array.

• Type `pad[1] = 0`

  1st element of pad array

• To verify the array, type `da` (display array)
• To define our armaged TH 1D experiment we need to know three things...

1) Overall time of experiment
2) Rate of individual experiments
3) Length of single experiment

• Example:

  > Overall time: 4 hrs, 4 x 3600 s = 14400 s

  > Rate: Want 40 points over 4 hrs

  \[
  \frac{14400 \text{ s}}{40} = 360 \text{ s}
  \]
  
  Time between exps

  > Length of Exp: 6 s/scan x 16 scans = 96 s

  Use time command
• Thus:

Time between exps = 360 s
Time of single exp = 96 s

\[ \Delta = 360 - 96 = 264 s \]

pad between exps

• To set the pad array:

\[
\text{array ('pad', 41, 264, 0)} \]

Why 41?

pad [1] = 0
• Consider the simple case:

  \[ \text{Exp time} = 1 \text{s} \]

  \[ \text{Exp rate} = 1/\text{min} \Rightarrow \text{Once every 60s} \]

  \[ \Delta = 60 - 1 = 59 \text{s} = \text{pad} \]

  \[ \text{Total exp time} = 3 \text{ min} = 180 \text{s} \]

• Begin with \( \sim 180 \text{s total} \)

  \[ \text{array('pad', 3, 59, 0)} \]

  \[ \text{pad = 59, 59, 59} \]

  \[ \begin{array}{cccc}
  59 & 1 & 59 & 1 \\
  59 & 1 & 59 & 1 \\
  59 & 1 & 59 & 1 \\
  \end{array} \]

  \[ t = 0 \quad \frac{\text{3 min}}{} \]

  \[ t = 1 \quad 2 \quad 3 \]
• Now with pad[1] = 0

<table>
<thead>
<tr>
<th>0s</th>
<th>1s</th>
<th>59s</th>
<th>1s</th>
<th>59s</th>
<th>1s</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td></td>
<td>2</td>
<td></td>
<td>3</td>
</tr>
</tbody>
</table>

• Thus, generally add 1 element to array

```python
array(['pad', 4, 59, 0])
```
• HW for Friday, 2/9:

- Assume time per transient = 6s
- Assume need nt = 32
- Assume rate: 10/hr
- Assume total time = 8 hrs

Set up pad array - show calex