NMR Spectroscopy for Chemical Reaction Kinetics

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NMR for *in situ* reaction studies

- Advantages of NMR for *in situ* study of reaction kinetics (aside from the obvious)
  - Compatible with many inert materials of construction (borosilicate glass, quartz, alumina, zirconia, fluoropolymer)
    * Enables operation at P from vacuum to > 10,000 psi
  - Compatible with wide temperature ranges (commercial probes available with ranges -100 – 500 °C)
  - Ability to function with mg quantities of reagents in closed vessels permits safe use of highly toxic or reactive species
  - Advances in processing software enable facile generation of conc. v. time plots
Sealed, thermostatted ampule

- A design suitable for careful kinetic studies – 10 mm ampule with 5 mm neck, flame-sealed after charging. Ampule resides below top of probe Dewar, minimizing temperature gradient.
- Well-suited for gas-phase reactions, or liquid-phase at positive pressure.

Common experimental challenges

- Use of deuterated solvent for field-frequency lock is often not possible or convenient, so field drift is observed in spectra.
- Probe electronics often not at thermal equilibrium at start of a reaction, resulting in changing signal phase with time.
Example #1: Decomposition of gaseous di-t-butyl peroxide

- DTBP is a common thermal and photochemical initiator in both liquid and gas phase.

Clean, ideal chemistry (for this study!)

Complications
Example #1: Decomposition of gaseous di-\(t\)-butyl peroxide

- Kinetic \(^1\)H NMR spectra (400 MHz), 150 °C, 16 h
Example #1: Decomposition of gaseous di-t-butyl peroxide

- Phase correction of individual spectra
Example #1: Decomposition of gaseous di-t-butyl peroxide

- Manual correction of integral ranges for drift
Example #1: Decomposition of gaseous di-t-butyl peroxide

- Derivation of first-order rate constant
Example #1: Decomposition of gaseous di-\textit{t}-butyl peroxide

- Arrhenius parameters: $E_a = 35.1$ kcal/mol, $\log A = 14.3$

\[
y = -17486x + 32.437
\]

$R^2 = 0.9989$
Example #2: Isomerization of quadricyclane

- Thermally-induced gas-phase isomerization:

$^1$H kinetic series, 400 MHz

$172 \, ^\circ \mathrm{C}$

8 h
Example #2: Isomerization of quadricyclane

- $^{13}$C, 1 atm quadricyclane, n.i.a.

$^{13}$C{$^{1}$H} kinetic series, 100 MHz

$172 \, ^\circ \text{C}$

$8 \, \text{h}$

$2.25 \times 10^{-4}$ by $^{1}$H

$2.40 \times 10^{-4}$ by $^{1}$H
Example #3: Diels-Alder addition of maleic anhydride to butadiene

- Classic overall 2\textsuperscript{nd}-order reaction:

\[ \text{H} \quad \text{H} \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{H} \quad \text{H} \quad \text{O} \quad \text{O} \quad + \quad \text{H} \quad \text{H} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{80 °C} \quad \text{C}_6\text{D}_6 \]

- Spectrus accommodates 2A $\rightarrow$ P, or A + B $\rightarrow$ P if $[A]_0 = [B]_0$
Example #3: Diels-Alder addition of maleic anhydride to butadiene

- Kinetic $^1$H NMR spectra, 400 MHz
Example #3: Diels-Alder addition of maleic anhydride to butadiene

- Easy export of integral intensity v. time data
Summary

• *In situ* studies of reaction kinetics by NMR spectroscopy is a safe and experimentally-flexible means of probing both liquid and gas-phase reaction systems.

• Advances in spectral processing software permit facile phase and frequency drift corrections, reducing time required for data analysis.