

## 4. Studying Dynamic Processes by NMR

- **Intramolecular processes**

- rotations (M-C, M-M, C-C or other bonds)
- skeletal rearrangements
- ring whizzing (migration of metal on  $\eta^1$ -C<sub>5</sub>H<sub>5</sub> rings)
- hapticity changes ( $\eta^1 \rightarrow \eta^3$ )
- bridge-terminal exchange (eg. CO complexes)

- **Intermolecular processes**

- Ligand exchange (dissociation / re-association):
  - $J_{XY}$  coupling *completely lost* if the X-Y bond breaks
  - $J_{XY}$  coupling *averaged* if X-Y bond retained

**But...how do we know a dynamic process is operative?**

- broadened lines
- temperature dependence
- field dependence
- spectra that are too simple or too complicated for expected structure

**What we see in the spectrum of a dynamic system depends on the particular dynamic process involved and the rate constants associated with it, the temperature and the magnetic field of the NMR instrument.**

However, for any process there are three distinct temperature regimes:

**Slow exchange (Fig 1a)**

$$T < T_c$$

$$k \ll \delta\nu$$

- distinct resonances are observed for the exchanging partners

**Coalescence (Fig 1c)**

$$T = T_c$$

$$k \approx \delta\nu$$

- exchanging resonances just merge into a single broad peak

**Fast exchange (Fig 1e)**

$$T > T_c$$

$$k \gg \delta\nu$$

- a weighted average signal is observed for the exchanging resonances

where  $T_c$  = coalescence T,  $k$  is the rate constant and  $\delta\nu$  is the separation of the exchanging resonances at the low T limit in Hz

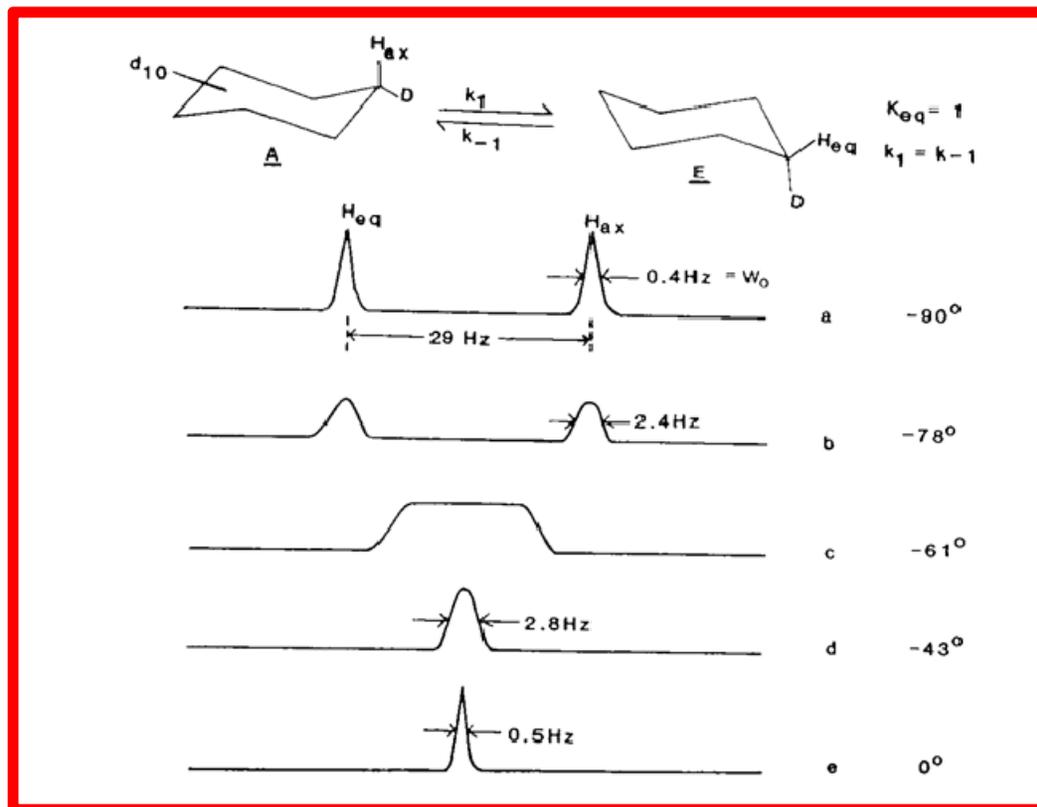


Figure 1 Axial-equatorial exchange in cyclohexane-d<sub>11</sub>

## Extraction of rate data from the spectra: equal population, 2-site exchange

**Note:** For a simple *equal-population, 2-site* exchange process like that in Fig. 1, there are straightforward mathematical formulas linking  $\delta\nu$  and **line widths** to **k**. In any other situation the extraction of rate data is more complex and usually requires computer simulation.

**Slow exchange regime:**  $k = \pi(w-w_0)$

- where  $w_0$  is the width at half height of the peak at the low T limit (0.4 Hz in Fig 1a) and  $w$  is the width of the peak at the T in question (2.4 Hz)

**At coalescence:**  $k = \pi(\delta\nu)(2)^{-1/2}$

- where  $\delta\nu$  is the chemical shift difference between the resonances in the low T limit (29 Hz in Fig 1a)

**Fast exchange regime:**  $k = \pi(\delta\nu)^2(w-w_f)^{-1}(2)^{-1/2}$

- where  $w$  is the width of the resonance at T (eg. 2.8 Hz in Fig 1d) and  $w_f$  is the width of the resonance at the fast exchange limit (0.5 Hz in Fig 1e)

## Calculating activation parameters from rate data:

**Eyring equation:**

$$k = (k_b T/h) e^{-\Delta G^*/RT}$$

therefore

$$\Delta G^* = -RT[\ln(k/T) + \ln(h/k_b)]$$

and

$$k = (k_b T/h) e^{-\Delta H^*/RT} e^{\Delta S^*/R}$$

more usefully:

$$\ln(k/T) = -\Delta H^*/RT + [\Delta S^*/R - \ln(h/k_b)]$$

so a plot of  $\ln(k/T)$  versus  $1/T$  is a **straight line** for which:

$$\Delta H^* = -(\text{slope})R$$

and

$$\Delta S^* = [\text{intercept} + \ln(h/k_b)]R$$

$\Delta G^*$  can be obtained directly at the coalescence temperature  $T_c$  using the formula given below:

$$\Delta G^* = (1.912 \times 10^{-2})(T_c)[9.972 + \log(T_c/\delta\nu)] \quad \text{in kJ/mol}$$

where  $T_c$  is in K and  $\delta\nu$  is in Hz

For the example in Fig 1, the following rates can be calculated using the appropriate formula:

$$k_{-78} = \pi(2.4-0.4) = 6.28 \text{ s}^{-1}$$

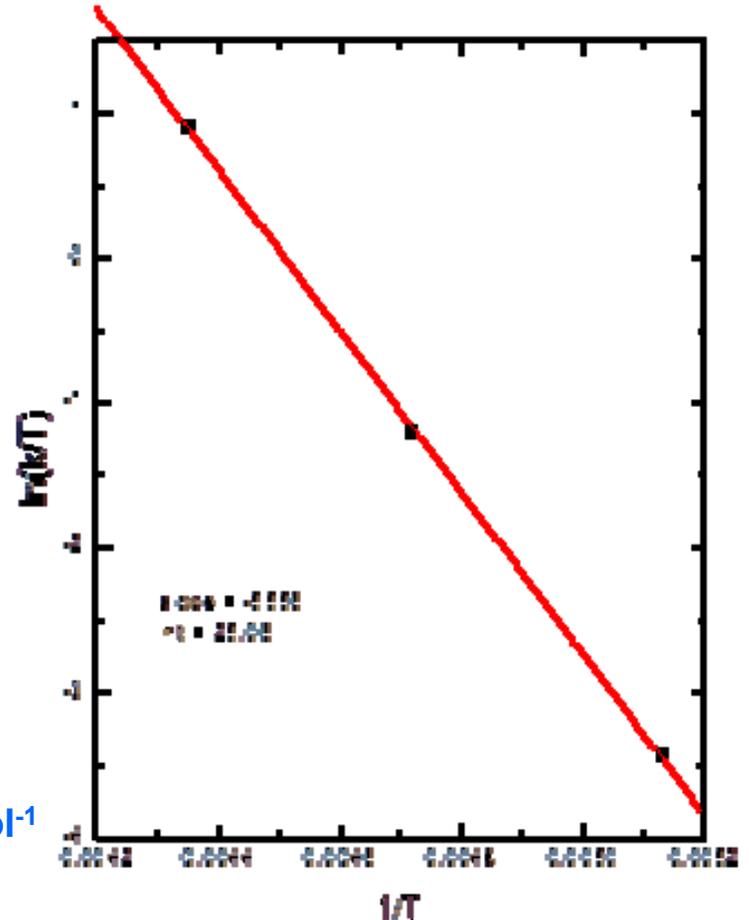
$$k_{-61} = \pi(29)(2)^{-1/2} = 64 \text{ s}^{-1} \text{ (coalescence temperature)}$$

$$k_{-43} = \pi(29)^2/(2)(2.8-0.5) = 566 \text{ s}^{-1}$$

From the Eyring plot:

$$\Delta H^* = -5556 \text{ K} * (8.314 \text{ J K}^{-1} \text{ mol}^{-1})/1000 = 46 \text{ kJ/mol}$$

$$\Delta S^* = [25.06 + \ln(h/k_b)] * 8.314 = (25.06-23.76) * 8.314 = 11 \text{ J K}^{-1} \text{ mol}^{-1}$$



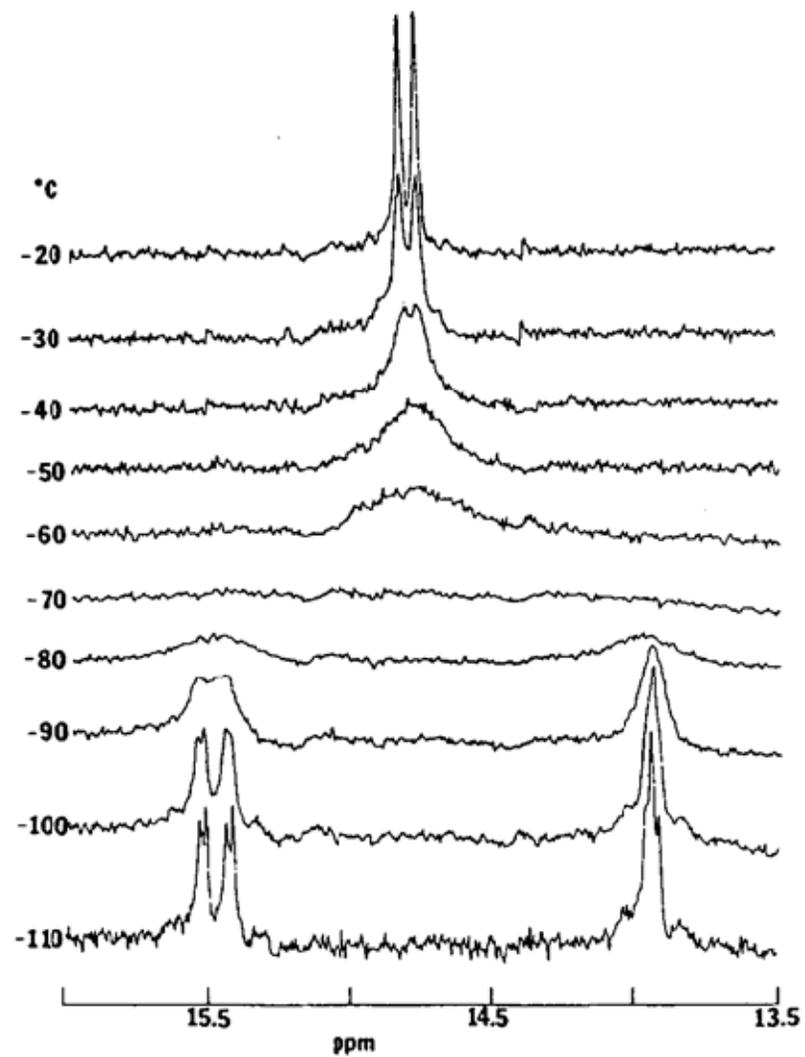
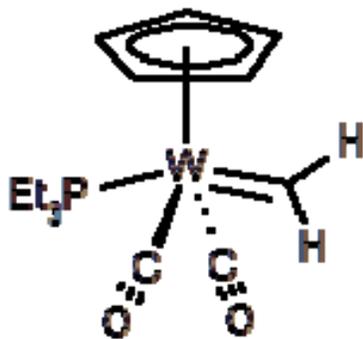
## Significance of $\Delta S^*$

- **Large positive values = less ordered transition state**
  - consistent with processes like ligand dissociation or bond breaking
- **Large negative values = more ordered transition state**
  - consistent with associative processes and bond making steps
  - also expected for highly ordered transition states such as a four-membered transition state  $\sigma$ -bond metathesis

However, getting reliable values of  $\Delta S^*$  requires many recording the NMR at a large number of temperatures because the error associated with the Eyring plot is large.

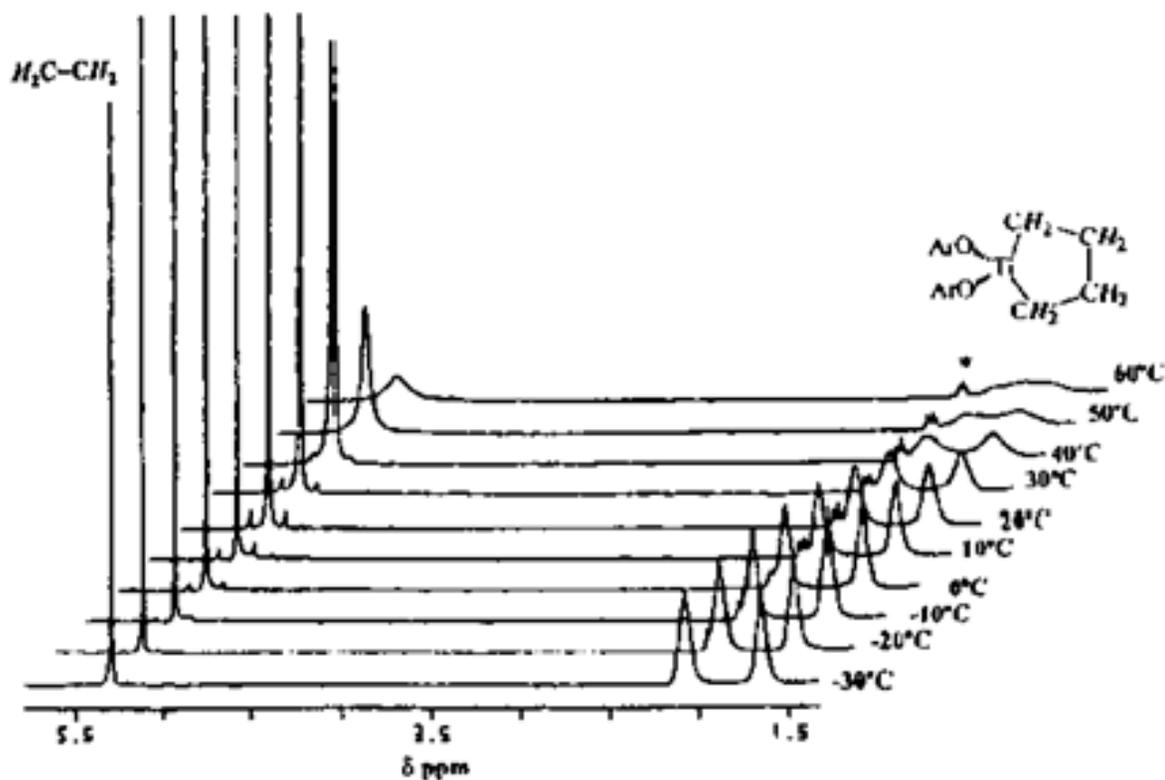
## Organometallic examples:

a) *restricted rotation about a bond*



b) exchange with free ligand

Ethylene exchange with a titanacyclopentane



**Figure 1.** <sup>1</sup>H NMR (200 MHz) spectra of [Ti(OC<sub>6</sub>H<sub>3</sub>Ph<sub>2</sub>-2,6)<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>] (4) and ethylene in C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub> solvent (\* indicates protio impurity) over the temperature range -30 to +60 °C.

### Scheme 4

