

**Purpose:** The barrier to rotation ( $E_a$ ) in N, N-dimethylacetamide (N,N-DMA) is determined by measuring the rate constants for cis-trans isomerization by changes in NMR line shapes as a function of temperature.

This is a modified version of the procedure given in the document: “NMR Determination of the Rotational Barrier in N,N-dimethylacetamide” by:

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A corrected version of the original paper published in J. Chem. Ed. was downloaded from: <http://www.colby.edu/chemistry/PChem/lab/NMRrotBarrier.pdf>, and is a separate document accompanying this one.

### Experimental Procedure

Sample preparation will be handled by the Instructor. The measurement will be made in the NMR facility with assistance from the Manager. The NMR spectrum will be measured at 10 or 20 °C increments from 290 K to about 380 K. From the peak widths and frequencies of the inequivalent methyl hydrogens attached to N at each temperature, the rate of cis-trans isomerization is calculated at each temperature, using the equation given at the bottom of this page.

### Calculations

The temperature in this experiment is never low enough to observe the slow exchange limit. For the value of  $\Delta\nu_0$ , which is slightly larger than the room temperature value of the peak separation, use  $77 \text{ sec}^{-1}$ . The data fall into three groups corresponding to intermediate exchange, coalescence, and fast exchange.

The authors state that the equations 8, 9, 10, 11, and 13 are approximate forms of the more exact equation 4. We, however, will make Equation 4 more transparent by simply **multiplying the top and bottom** by the exchange rate constant,  $k_{\text{ex}}$ , (Note that  $k_{\text{ex}}$  is the same as  $k$  and that the “lifetime”  $\tau=1/k$ ) This gives the following equation for  $g(\nu)$ , **which is just the intensity in arbitrary units at a given frequency**:

$$g(\nu) = \frac{K(\nu_A - \nu_B)^2}{k[0.5(\nu_A + \nu_B) - \nu]^2 + 4\pi^2 k^{-1}[(\nu_A - \nu)^2(\nu_B - \nu)^2]}$$

Note that now the exchange rate,  $k$ , is out of the numerator, and **multiplies** the left term of the denominator (the resonance term of the average of the two separated lines), but **divides** the right hand term, which is the product of the individual A and B resonance terms. It is now easy to see that when  $k$  is small, the right hand term will dominate, and two peaks will be predicted: one when  $\nu = \nu_A$  and one when  $\nu = \nu_B$ . If  $k$  is large, however, then the left term will dominate, and the peak will come when  $\nu = 0.5(\nu_A + \nu_B)$ , i.e. the average of the two individual peaks.

This equation can easily be entered into column C of an Excel sheet as

$$=KK*(\text{nua}-\text{nub})^2 / (\text{kex}*(0.5*(\text{nua}+\text{nub})-\text{B1})^2+4*\text{PI}()^2*\text{kex}^{-1}*(\text{nua}-\text{B1})^2*(\text{nub}-\text{B1})^2)$$

where column B will hold a range of frequencies in hz, with 0.1 hz increments. KK is any constant to vary the height conveniently if needed. The convenient name tags nua, nub, kex, etc., may be defined in excel with the following:

1. type tau, kex, nua, nub, KK, nu down a column starting for example at E1
2. select those cells and the cells just to their right.
3. click formulas, and choose "Create from selection"

(we must use kex for the rate of exchange because k by itself is reserved for some excel function)

Now typing tau will be equivalent to typing \$E\$1; typing kex will be equivalent to typing \$E\$2, etc.

Use the downfield (cis to carbonyl), peak of the doublet for your experimental measurements, to avoid the effects of coupling between the trans N-methyl group and the acetyl methyl group. NMR spectra are recorded in parts per million (ppm) of the nominal frequency in  $\text{s}^{-1}$  for H for the basic magnetic field at the sample. We are using the 500 Mhz instrument, therefore 1 ppm is 500 hz, and 3 ppm = 1500 hz.

The archaic terms "downfield" and "upfield" date to early times when the frequency was kept fixed and peaks were recorded by the field strength required to get resonance with the proton. A proton with high electron density (like methyl hydrogens) is strongly shielded by currents that **oppose** the applied field (called *shielding*). The higher the electron density, the lower actual the field at the proton. A higher magnetic field therefore is needed for the proton to be in resonance with a given frequency. A lower applied field was needed for less shielded protons, such as that in an aldehyde. Aldehydes were therefore said to resonate downfield from methyl protons. In varying the field as is done today, the aldehyde proton resonates higher frequency (higher ppm), but is still said to be down field.

The spectra from the instrument should be exported as "ascii" files (meaning "text").

## **Report**

Using an Excel spreadsheet, use the equation given above to obtain simulated spectra ( $g(\nu)$ ), i.e. frequencies and line widths. At each temperature, find a value of k that closely matches to your experimental spectrum. These are your "measured" rate constant ( $k$ ) values.

### **1. Arrhenius**

$$k_{\text{rate}} = A \exp(-E_a/RT)$$

Plot  $\ln k$  versus  $T^{-1}$  to determine the activation energy and pre-exponential factor for the rate constant for exchange (isomerization) according to the Arrhenius equation for rate constants:

Compare your results for the rate constants, A, and  $E_a$  to those in reference 1 of the attached document.

## 2. Absolute (Eyring)

With a similar plot suggested in the Gasparo document, use the “absolute” rate constant equation

$$k = \frac{k_B T}{h} e^{\frac{-\Delta H^\ddagger}{RT}} e^{\frac{\Delta S^\ddagger}{R}}$$

developed by Eyring and others to obtain  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ , the standard enthalpy and entropy of activation. ( $k_B$  is Boltzmann’s constant and  $h$  is Planck’s constant.

## 3. The Connection

Note that in solution  $\Delta H$  is essentially  $\Delta E$  (because  $\Delta V$  is very small). In that case, what does the absolute equation give for the Arrhenius preexponential factor at 298 K if the  $\Delta S^\ddagger$  is 0,  $-10 \text{ JK}^{-1}$  and  $+10 \text{ JK}^{-1}$ ?

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