

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.

General Procedure: We use a theoretical equation to calculate the spectrum as a function of temperature. By varying the resonant frequencies, and the exchange rate constant for cis-trans flipping, k , until the calculated spectrum matches the observed spectrum, k is determined at each temperature. The Arrhenius activation energy is then found from plotting $\ln k$ vs. $1/T$.

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

Francis P. Gasparro, Department of Biochemical Sciences, Princeton University, Princeton, New Jersey 08540 and Nancy H. Kolodny, Wellesley College, Wellesley, Massachusetts 02181,

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 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 are going to use **only** Equation 4, but we will make it more transparent by simply **multiplying the top and bottom** by the exchange rate constant, k_{ex} , (Note that k_{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 applied radio frequency, ν** :

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

Note that this equation gives **spectral peaks 3 ways**: whenever $\nu = \nu_A$, or $\nu = \nu_B$, or $\nu = \nu_A + \nu_B$, depending on whether the exchange rate, k , is large or small.

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.

Spread Sheet

Enter the above equation into column C of an Excel sheet at row 12 as:

$$=KK*(nua-nub)^2 / (kex*(0.5*(nua+nub)-B12)^2+4*PI()^2*kex^-1*(nua-B12)^2*(nub-B12)^2),$$

where column B will hold a range of frequencies in hz, with 0.1 hz increments starting at about 1200 hz and ending at about 1900 hz. KK is any constant to vary the height conveniently if needed. The convenient **name tags**, nua, nub, kex, etc., may be defined in excel by 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 τ ; typing kex will be equivalent to typing k , etc. You will vary only kex, nua, nub, and maybe KK. Tau is determined as $1/kex$, i.e., $1/\tau$.

Parts per million, "Downfield", "Upfield"

NMR spectra are recorded in parts per million (ppm) of the nominal frequency in s^{-1} for H for the basic magnetic field at the sample. The chemical shift for the NMR peak of a proton in a particular chemical environment is independent of the strength of the applied magnetic field.

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 in a high electron density (like methyl hydrogens) is strongly *shielded* by currents that **oppose** the applied field.

Therefore, the higher the electron density, the lower will be the actual 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 frequency, as is done today, the aldehyde proton resonates at **higher frequency** (higher ppm), but is still often said to be **downfield**.

The spectra from the instrument should be exported as “ascii” files (meaning “.txt”).

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.

Finding the activation energy

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

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

(Equation 17 of Gasparo)

developed by Eyring and others to obtain ΔH^\ddagger and ΔS^\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 ΔH is essentially ΔE (because ΔV is very small *in solution*).

(*Not $E_a = \Delta H^\ddagger + m RT$ as stated by Gasparo, which is true for gas phase only.*) In that case, what does the absolute equation give for the Arrhenius preexponential factor at 298 K if the ΔS^\ddagger is 0, -10 JK⁻¹ and +10 JK⁻¹?
