

Experiment 7

NMR Determination of Keto-Enol Equilibrium Constants

Adapted from *Experiments in Physical Chemistry* by Garland *et al.*, 8th, Experiment 42, p. 466

1 Introduction

In this experiment, you will be using Nuclear Magnetic Resonance (NMR) to determine the equilibrium compositions, equilibrium constants (K_e), and the standard free energy differences (ΔG_o) within three Keto-Enol mixtures.

A chemical equilibrium between a **keto** form (a ketone or an aldehyde) and an **enol** (an alcohol) is referred to as **keto-enol** tautomerism. The interconversion of the two forms involves the movement of a hydrogen atom and the shifting of bonding electrons. For example, movement of one of the protons in one of the CH_3 groups on acetone (the main constituent in fingernail polish remover), to the oxygen atom, results in an unsaturated alcohol. Although, the keto form is by far the most prevalent form in acetone, the enol form can be enhanced through intra-molecular hydrogen bonding effects (bonding with other molecules), as well as conjugation, particularly for heavier molecular weight ketones. Proton NMR can easily distinguish these isomers apart, since the migrating proton experiences very different chemical environments (CH_3 and OH). Indeed, NMR can provide relative concentrations of all protons present, from which equilibrium constants, etc, can be derived.

2 Theory

See the *Theory* section of Experiment 42 on p. 466 for a detailed discussion of the theory behind this experiment. You will need to read this section in order to understand how NMR can reveal Keto-Enol equilibrium constants.

3 Experimental procedure

Follow the directions outlined in the section *Experimental* of the Experiment 42 on p. 472 in the text. Your TA will supply you with instructions on how

to operate the NMR instrument. The NMR temperature is 29.5°C.

You will be using Carbon Tetrachloride and Tetramethyl Silane (TMS). Since both are toxic, these must be handled with care, i.e. solutions must be prepared in one of the fume hoods.

Also, since TMS has a low boiling point, this is stored in the refrigerator in the stock room (please return this as soon as possible).

The success of this experiment depends on the care in which the measurement and computations are carried out.

4 Calculations and Discussion

Carry out all calculations called for in *Calculations* section of the text. You should calculate K_e values from *both* the $-\text{CH}_3(\text{enol}) / -\text{CH}_3(\text{keto})$ ratios and the $=\text{CH}(\text{enol}) / -\text{CH}_2(\text{keto})$ ratios. In the second case, note that the $-\text{CH}_2$ peaks represent twice as many hydrogen atoms as the $=\text{CH}$ peaks. Calculate the ratios of $-\text{CH}_3$ intensities to the $=\text{CH}$ and $-\text{CH}_2$ intensities (as called for in the text) *only* if all integrations have been carried out with the same instrument scale. Otherwise, ignore this calculation except to note rough ratios from peak heights. Address all the issues raised in the *Discussion* section of the text in writing your report.

NMR Instrument Operations

- 1) Load prepared sample into the NMR
- 2) Open PNMR-H1 icon
- 3) Type **shim** and press enter on the *H1>* command line
- 4) Type relaxation delay of **2**, press enter and wait for spectrometer to shim (a gray box will disappear when finished)
- 5) Verify the parameters:
Type **si** (size of the buffer), press enter, type **8k**, press enter
Type **ns** (number of scans), press enter, type **8**, press enter
Type **rd** (relaxation delay), press enter, type **2**, press enter
Type **w1** (pulse width), press enter, type **1400**, press enter
- 6) Type **zg**, press enter and type a file name, press enter
- 7) *If FID is red, press Ctrl-K to stop, type **rg** (relaxation delay), press enter and use a smaller value of relaxation delay, i.e. 1, press enter. Then type **zg** press enter to start collecting the spectrum. You can overwrite the old file.*
- 8) Once 8 scans had been collected the gray box will disappear, minimize the PNMR window and open the Nuts program by clicking its icon on the desktop
- 9) Type **a2** without pressing enter to load the spectrum
- 10) *Note: NUTS uses two-letter commands and does not require pressing the enter key. A command is executed once you type two letters.*
- 11) Type **ap** to autophase the spectrum.
- 12) Click and hold the left mouse button on the TMS peak (1st peak from right) and press **O**. A window should pop up which allows you to offset the whole spectrum. The value of the TMS shift should be highlighted – Horizontal Dimension, Point values in ppm. Change this to zero and click OK to shift the spectrum. The TMS peak should be at zero now.
- 13) Type **pp** to automatically label the peaks.
- 14) If some peaks were not labeled type **dp** and click those peaks. Press **t** to add these peaks to the table. Press **enter** when finished.
- 15) Type **id** to integrate the NMR spectrum
 - a. Click the left mouse button twice on left side of the peak then once on the right side.
 - b. Repeat until you have integrated the intensities of all the peaks in the spectrum.
 - c. Click once on either the keto or enol peak then click **v** and enter 2 or 1, respectively. Recall that in 1H-NMR spectra, relative signal integrations (i.e. the area under the signals) are proportional to the number of equivalent H atoms giving rise to that signal.
 - d. Press enter to exit the ID mode.
- 16) Type **cb** to display a table listing the peaks in your spectrum.