

Lab #5 - NMR Determination of Keto-Enol Equilibrium

Objective

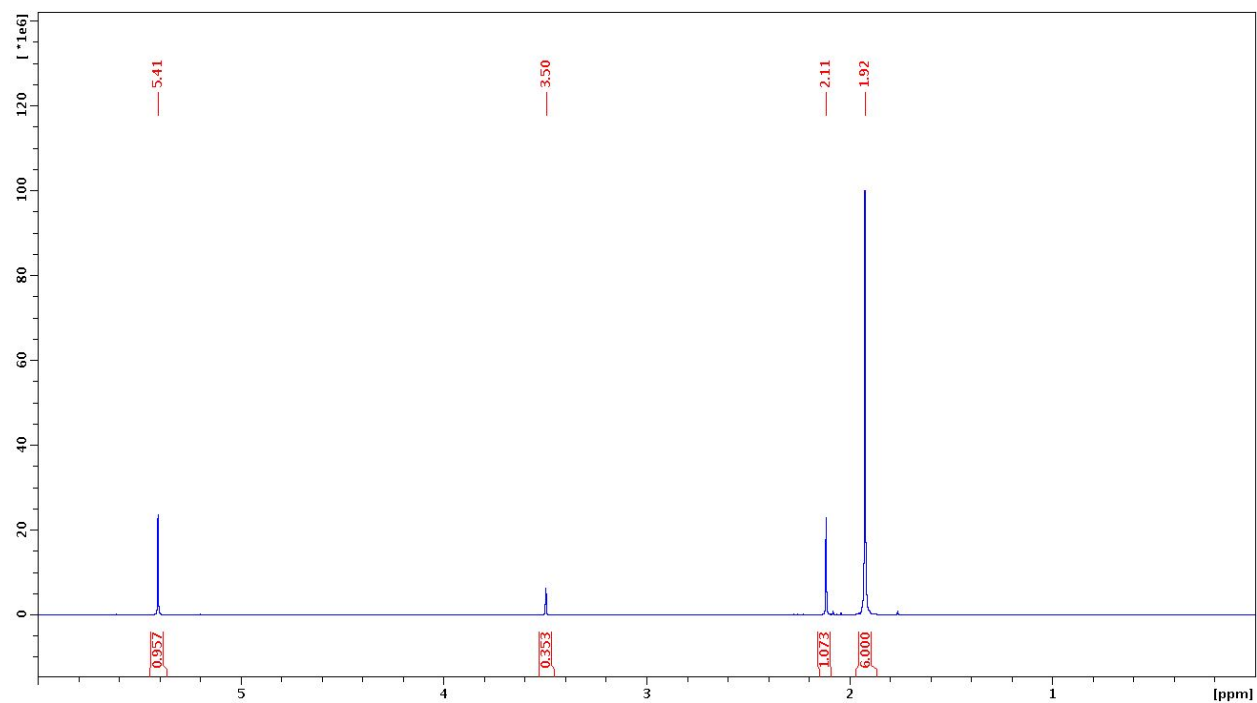
To use NMR spectroscopy to determine the equilibrium and kinetics of a keto-enol equilibrium. In this experiment, the keto-enol equilibrium for β -diketones and β -ketoesters due to the : acetylacetone and ethyl acetoacetate. We will analyze the NMR measurements, measuring chemical shifts and spin-splitting patterns to assign protons and determine the prevalence of enol formation and the equilibrium of the keto-enol reaction.

Methods

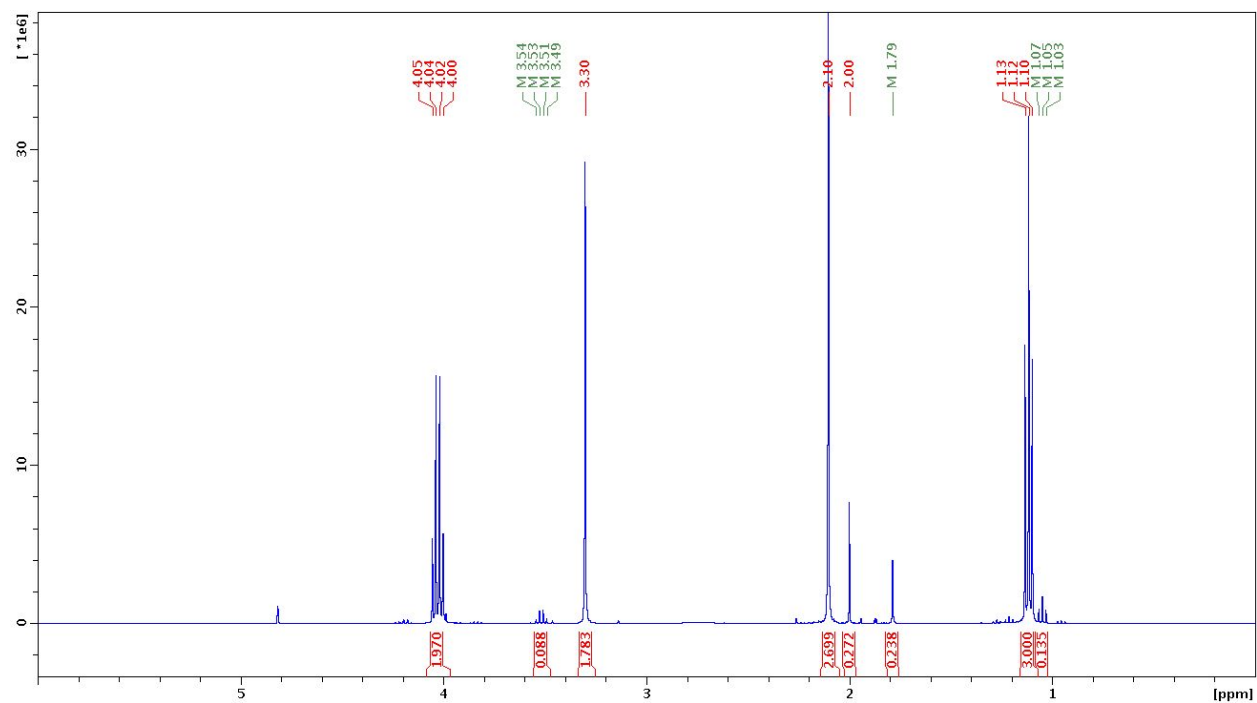
A β -diketone and β -ketoester are used because their delocalized electron complex allows for the oxygen of one ketone to protonate, and the electronegativity of the second oxygen helps maintain the complex. The electrons shared with hydrogen on the outer carbons are able to be formed due to the basic component of the solution, which stabilizes the alkene bond and allows for sufficient deprotonation. The rate determining step of this reaction is the first step of the enol formation.

Portions of ethyl acetoacetate and acetylacetone (*0.0095 mol; 0.76 mL acetylacetone, 0.39 mL ethyl acetoacetate*) are separated into four solutions; two of each portions are prepared. Each of the solutions are introduced to deuterated chloroform and deuterated methanol (*0.0005 mol; 0.05 mL CDCl₃; 0.06 mL CH₃COD*). The primary purpose of using deuterated solutions is because the NMR machine measures the absorption strength of the deuterium solvent. These will be prepared for NMR spectroscopy.

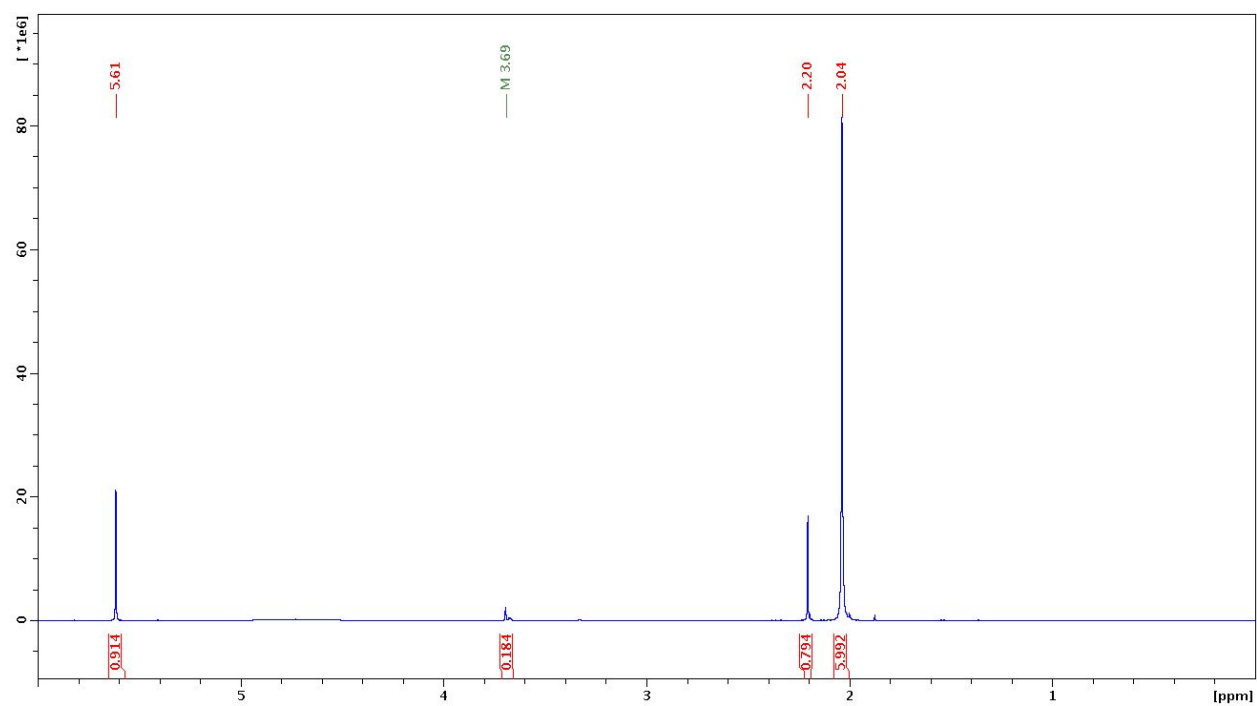
NMR Results for Acetylacetone in Deuterated Chloroform



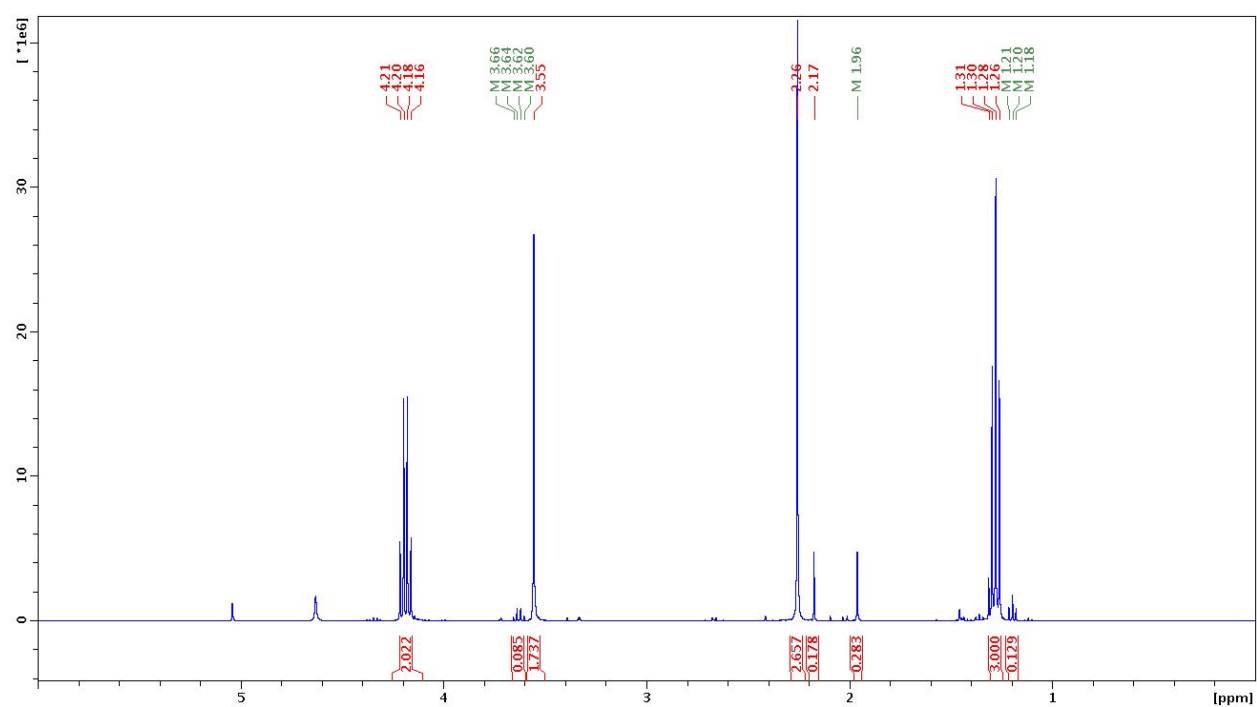
NMR Results for Ethyl Acetoacetate in Deuterated Chloroform



NMR Results for Acetylacetone in Deuterated Methanol



NMR Results for Ethyl Acetoacetate in Deuterated Methanol



Discussion

For *acetylacetone*, we should expect an ^1H NMR shift at about 3.5 ppm for the CH_2 hydrogen, present on the carbon between the two ketones. The ^1H NMR shift for the enol form of acetylacetone should appear around 5.5 ppm, as the absorption increases as the electrons delocalize.¹

The observed integration at the described shifts for acetylacetone in deuterated chloroform and deuterated methanol are tabulated below:

Acetylacetone HNMR Integration Values

	Acetylacetone in Deuterated Chloroform	Acetylacetone in Deuterated Methanol
Ketone integration (~3.5 ppm)	0.353	0.184
Enol integration(~5.5 ppm)	0.957	0.913

For *ethyl acetoacetate*, we should expect the ^1H NMR for the CH_3 hydrogen on the end carbon at about 2.2 ppm, while ^1H NMR on the CH_2 hydrogen of the enolate at around 4.1 ppm.¹ These are tabulated below:

Ethyl Acetoacetate HNMR Integration Values

	Ethyl acetoacetate in Deuterated Chloroform	Ethyl acetoacetate in Deuterated Methanol
Ketone integration (~2.2 ppm)	2.699	2.657
Enol integration(~4.1 ppm)	1.970	2.022

The integration intensities measured by the NMR machine can determine for us the presence of the ketones and enols within the complex. The ratio of ketones and enols in this complex will be determined using the intensity ratios.

Ratio of enol formation of acetylacetone in Deuterated Chloroform:

$$\text{Ratio } K_E = \text{enol} \div \text{keto} = 0.957 \div (0.957 + (0.353 \div 2)) = \mathbf{0.84 = 84\% \text{ enol/keto}}$$

Ratio of enol formation of acetylacetone in Deuterated Methanol:

$$\text{Ratio } K_E = \text{enol} \div \text{keto} = 0.913 \div (0.913 + (0.184 \div 2)) = 0.91 = 91\% \text{ enol/keto}$$

Ratio of enol formation of ethyl acetoacetate in Deuterated Chloroform:

$$\text{Ratio } K_E = \text{enol} \div \text{keto} = (1.970 \div 2) \div ((1.970 \div 2) + (2.699 \div 3)) = 0.52 = 52\% \text{ enol/keto}$$

Ratio of enol formation of ethyl acetoacetate in Deuterated Methanol:

$$\text{Ratio } K_E = \text{enol} \div \text{keto} = (2.022 \div 2) \div ((2.022 \div 2) + (2.657 \div 3)) = 0.53 = 53\% \text{ enol/keto}$$

The free energy of the enol reaction can be determined using the Gibbs free energy equation, shown below:

$$dG = R \cdot T \cdot \ln(k)$$

Where dG, or delta G, represents the available free energy for the reaction to occur, the R represents the gas constant, T is temperature in Kelvin, and k is a dissociation constant which our reaction ratios will be used. The results for determining the Gibbs free energy by the dissociation ratio is tabulated below:

	acetylacetone	ethyl acetoacetate
Deuterated Chloroform	431 J/mol	1620 J/mol
Deuterated Methanol	233 J/mol	1572 J/mol

The keto-enol relationship determined for acetylacetone resembles a similar experiment performed by Drexler and Field in 1976, albeit under hotter conditions- the percent enol concentration by weight volume was high (over 80%) as decreased as the percent weight of acetylacetone increased, likely due to the nature of the complex formation.¹

Conclusion

This lab successfully demonstrates the value of using NMR to determine the effective ratio of components by measurement of peak intensity. By determining which hydrogen

structure forms which peak, the prevalence of the enol structure signal in comparison to the ketone structure signal can help us determine the equilibrium ratio of the keto-enol complex. in this case, the equilibrium ratio can be used within the Gibbs free energy equation to determine the free energy available within the system and the spontaneity of the reaction can be analyzed and determined.

References

1. Drexler, Edward J., and Kurt W. Field. "An NMR Study of Keto-Enol Tautomerism in β -Dicarbonyl Compounds." *Journal of Chemical Education*, vol. 53, no. 6, 1976, p. 392., doi:10.1021/ed053p392.
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