Solvent and Temperature Effects on Tautomeric Equilibria in Two β-Dicarbonyls

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ABSTRACT

This research used H-NMR to explore the equilibrium changes with temperature and solvent for acetylacetone, and compared to the equilibrium the dicarbonyl, ethyl acetoacetate. Two sets of acetylacetone scans, one solvated in deuterated chloroform and the second set in deuterated methanol, with four scans per set, were analyzed from provided Free Induction Decay (FID) data files. For each set, there was an FID for scans at 25, 35, 45, and 55° C. A single scan was analyzed from a furnished FID, ethyl acetoacetate, in deuterated chloroform run at 25° C. For acetoacetone data, the equilibria were computed for both sets of solvation. The two sets had equilibria strongly toward the enol side of the equilibrium. The CD_3OD solvated acetylacetone having equilibrium constants (K_c) from 2.97 – 2.00 and the $CDCl_3$ solvated scans with K_cs from 5.88-4.35. A regression was performed for each set on a van't Hoff plot, of $\ln(K_c)$ versus inverse temperature (1/K°). This produced a linear regression of $y = -907.43x + 1.2762$ for the $CDCl_3$ scans and $y = -1272.8x + 3.1692$ for the CD_3OD scans, from which thermodynamic values were derived. The $CDCl_3$ solvated scans showed a standard enthalpy of 7.545 kJ/mol, an entropy of 10.61 J/mol-K, and a Gibbs Free energy of 2.730 kJ/mol. The scans run so in CD_3OD, showed a standard enthalpy of 10.583 kJ/mol, an entropy of 26.350 J/mol-K, and a Gibbs Free energy of 4.383 kJ/mol.

In both scan sets, there was a shift toward the keto form as the temperature rose due to an increase in entropy and to protic solvent interference with the intramolecular hydrogen bonding that stabilize acetylacetone's enol form. The enol form was less prevalent in deuterated methanol than in deuterated chloroform, despite the lower solvent polarity of the chloroform. This is thought to be due to the interference with intramolecular hydrogen bonding by intermolecular hydrogen bonding, stabilizing the carbonyl preventing formation of the hydroxyl as part of the enol conversion.

Compared to acetylacetone, ethyl acetoacetate shows an enol-keto equilibrium strongly shifted to the keto side of the equilibrium, due to the carboxyl ester in the molecule. The K_c of ethyl acetoacetate was 0.10.

Key findings include that acetylacetone is heavily weighted to the enol side of the equilibrium, that a polar, protic solvent tends to shift the equilibrium more toward the keto form than an aprotic, less polar solvent, and that as the temperature rises the equilibrium shifts more toward the keto form.

1.0 INTRODUCTION

Tautomeric equilibria in β-dicarbonyl compounds are influenced by both temperature and solvent properties. Tautomerization, sometimes called desmotropism, involving the dynamic interconversion of isomers, as between keto and enol forms, is discernible by nuclear magnetic resonance (NMR). The equilibrium constant for this conversion is represented as K_c and is the concentration of the enol form divided by the concentration of the keto form. [1,2] Solvent and temperature environmental conditions play an important role in the ratio of

the keto and enol isomers in β-dicarbonyls, like acetylacetone and ethyl acetoacetate as investigated in this study. Polar solvents can shift the equilibrium toward the enol configuration, while non-polar solvents will often shift them toward the keto form.[3] For instance, in nonpolar solvents, the keto form of acetylacetone is often favored, while in polar solvents, the enol form tends be stabilized due to enhanced solvation effects.[4] Temperature is another critical environmental factor influencing the equilibrium constants between tautomeric forms. The increased molecular kinetic energy of higher temperatures facilitates interconversion between the keto and enol isomers but at the cost of resolution between tautomeric forms, by complicating the NMR spectra and potentially obscuring the equilibrium rates. At reduced temperatures NMR studies have shown that keto and enol forms can be resolved better, yielding more accurate ratio determinations.[5,6] Acetylacetone shows significant shifts in the equilibrium between the enol and keto isomers with changes in chemical or physical environmental factors such as temperature or solvent polarity.[7]

In summary both temperature and solvent effects are critical in determining how acetylacetone and other β-dicarbonyl compounds keto-enol equilibrium are affected. The interplay of temperature variations and solvent polarity and hydrogen bonding lead to substantial changes in the relative tautomeric isomer population, which makes careful control of the environmental factors critical during experimental testing.

2.0 EXPERIMENTAL

2.1 Chemicals

This paper was based on provided H-NMR FID data files. No chemicals were directly involved in this research. The data file source was in the Chem 6190 folder on the desktop.

2.2 Equipment

This paper was based on provided H-NMR FID data files. No hardware was involved, directly, in this research.

The software used to process FID files was MNova MestreNova, version 10.0.2-15465, released 6/17/2015, by Mestrolab Research S.L.

2.3 Experimental Conditions

Environmental conditions of the scans this research is based on are three scans at 25° C, two scans at 35° C, two scans at 45° C, and two scans at 55° C. One set of 25 through 55°C scans was performed in the solvent CD_3OD, another set of 25 through 55° C scans was performed in the solvent $CDCl_3$, these were of acetylacetone. A single scan of ethyl acetoacetate was at 25°C and was performed in the solvent $CDCl_3$.

2.4 Procedures

Nine FIDs were processed and analyzed. Each FID was first processed with a Fourier transform to convert them into a frequency domain plot. The plot was phase corrected, and the baseline is adjusted (apodization). The plot was zero adjusted to the tetramethylsilane (TMS) reference. After zero correction signal groups were selected and integrated, the largest being set to a value of one.

Once the groups were specified and integrated, then they were matched with the individual hydrogen containing chemical groups present on the molecule scanned. This involved utilizing the signal integral, the chemical shift of the signal, as well as the number of peaks per signal (multiplets). The latter relate to the number of hydrogens on neighbor carbons. A signal's integral ratio maps directly to the ratio of the number of hydrogens responsible for the signal, which is helpful in matching signals to the different compound groups.

Care was taken to ensure the spin-coupling constant, J, were the same between neighboring non-singlet signals, as a sanity check. These only applied to ethyl acetoacetate in the two β-dicarbonyls tested, given the acetylacetone signals were all singlets. Each signal should have n+1 peaks, where n is the number of hydrogens attached to beta neighboring carbons. If there are no neighboring carbons with hydrogens, n=0, such that there is a singlet signal, otherwise seen as only having one peak in the signal. [8]

In an H-NMR scan, the ratio of integrals is the ratio of the number group hydrogens. Once clear matching of signals to each compound's group is made, the number of the group's hydrogens can be calculated. Given the enol and keto forms both have signals in the scan, group integrals, one from the enol form, one from the keto form, will have a ratio that is also the ratio of tautomeric forms, scaling if that form's group don't have the same number of hydrogens. Dividing the normalized (for number of hydrogens) enol by keto groups, that are equivalent, yields the equilibrium constant for the conversion reaction (K_c) for that scan.

Four sets of scans were run for acetylacetone, a set per solvent ($CDCl_3$ and CD_3OD). In each set, a scan was at 25°, 35°, 45°, and 55° C were used to derive the enthalpy and entropy of the keto/enol tautomeric interconversion.

A linear regression of the inverse of the temperature in degrees Kelvin against the log natural of the equilibrium constant (K_c) was performed. The slope and x-intercept of the produced equation was used to determine the (ΔH) and entropy (ΔS) using **Equation 1**, **Equation 4**, and **Equation 5**. From those the Gibbs Free energy was calculated (ΔG) using **Equation 6**.

3.0 RESULTS AND DISCUSSION

3.1 Results

Nine NMR FID files were received. One FID corresponding to ethyl acetoacetate in $CDCl_3$ and two sets of four acetylacetone scan FIDs, one set in deuterated methanol (CD_3OD), and one set in deuterated chloroform ($CDCl_3$). These were processed: first by running a Fourier transform to get a spectrum; second, they were phase corrected; third, apodization was done; forth, the reference signal was used for zero adjustment; finally, signals were selected and integrated. The spectra and data were saved. Each set of acetylacetone spectra had scans at 25, 35, 45, and 55° C, for each solvent. The single ethyl acetoacetate spectrum was at 25°C, in $CDCl_3$.

For the two sets of acetylacetone spectra, using the chemical shift, the signals were mapped to the groups with hydrogens. These included both the enol and keto forms of the molecule, given both forms produced signals in the spectra. Below are the mappings made (group to signal) using the labels a, c, d, and e. The same labels will be on the scans correlating to signals.

	Keto ⟷ Enol					
acetylacetone	CH_3–CO–CH_2-CO-CH_3 ⟷			CH_3–COH=CH-CO-CH_3		
Signal Groups	d	c	d	e	a	e

The initial goal was to determine the ratio of keto to enol form. To do this the integrals for each signal group were obtained, then a representative signal group integral for the enol form was divided by a representative signal group integral, adjusted for differing numbers of hydrogens, for same carbon on the keto form. This quotient is the equilibrium constant, K_c, for the enol ⟷ ketone reaction. Groups d and e were used to represent the ketone and enol form, respectively. No hydroxyl group shows up in either scan, due to the narrow sweep width. It would normally be shown at approximately 15-16 ppm.[9] The corresponding enol/keto groups were chosen because they both had the same number of hydrogens, negating the need for scaling. Below are the tables including the integrals, equilibrium constants, and some derived computational values, with the corresponding temperatures.

Table 1 *Integral and Equilibrium data for $CDCl_3$ scans of acetylacetone*

$CDCl_3$		1/T	Integral	Integral	K_c	ln(K_c)
T (C°)	T (K°)	(1/K°)	e	d	e/d	ln(e/d)
25	298	0.00336	1.00	0.19	5.26	-1.6607
35	308	0.00325	1.00	0.20	5.00	-1.6094
45	318	0.00314	1.00	0.23	4.35	-1.4697
55	328	0.00305	1.00	0.23	4.35	-1.4697

Table 2 *Integral and Equilibrium data for CD_3OD scans of acetylacetone*

CD_3OD T (C°)	T (K°)	1/T (1/K°)	Integral e	Integral d	K_c e/d	ln(K_c) ln(e/d)
25	298	0.00336	1.00	0.34	2.94	-1.0788
35	308	0.00325	1.00	0.37	2.70	-0.9943
45	318	0.00314	1.00	0.43	2.32	-0.8440
55	328	0.00305	1.00	0.50	2.00	-0.6931

The clearest comparison of keto/enol equilibria variation, by temperature, is represented in percentage of enol versus keto form, as in **Table 3**.

Table 3 *Enol%*

T (K°)	CD_3OD	$CDCl_3$
298	74.6%	85.5%
308	73.0%	84.0%
318	69.9%	83.3%
328	66.7%	81.3%

The data for the 8 scans can be found in **Table 1**, in the reference section, which includes the integration values, both absolute and normalized, and signal range of each peak. The two solvent sets are arranged in parallel columns for easier comparison.

Equation 1

$$\ln(K_c) = -\frac{\Delta H}{R} * \frac{1}{T} + \frac{1}{R} * \Delta S$$

Plotting 1/T (K°) against the ln(K_c) we can get a linear regression, conforming to **Equation 2**.

Equation 2 *Equation of a line*

$$y = mx + c$$

Equation 3 *Slope is proportional to change in Enthalpy*

From the slope of the line, $m = -\frac{\Delta H°}{R}$

Yielding

Equation 4 *Change in Enthalpy*

$$\Delta H° = -m * R$$

and

Equation 5 *Change in Entropy*

Using the x-intercept, c, with the gas constant we get the change in entropy.

$$\Delta S° = c * R$$

Equation 6 *Gibbs Free Energy*

$$\Delta G° = \Delta H° - \Delta S° * T$$

Using the equations 1 – 5 above, we have a path to getting the change in enthalpy (ΔH) and the change in entropy (ΔS) with respect to temperature. [10]

Plotting the data from **Table 1** and **Table 2** we get the following two van't Hoff plots and linear regressions in **Figure 1** and **Figure 2**:

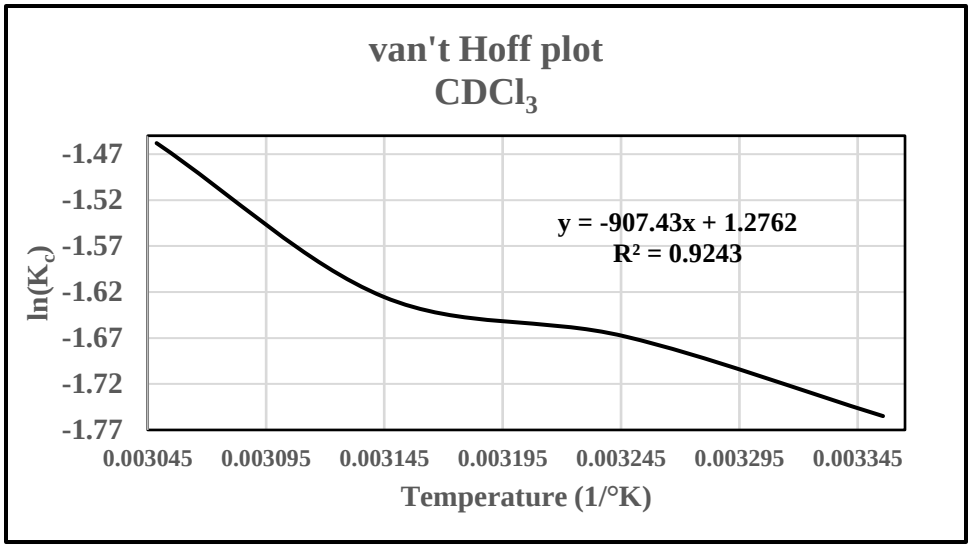


Figure 1 van't Hoff plot for acetylacetone NMR plots in $CDCl_3$

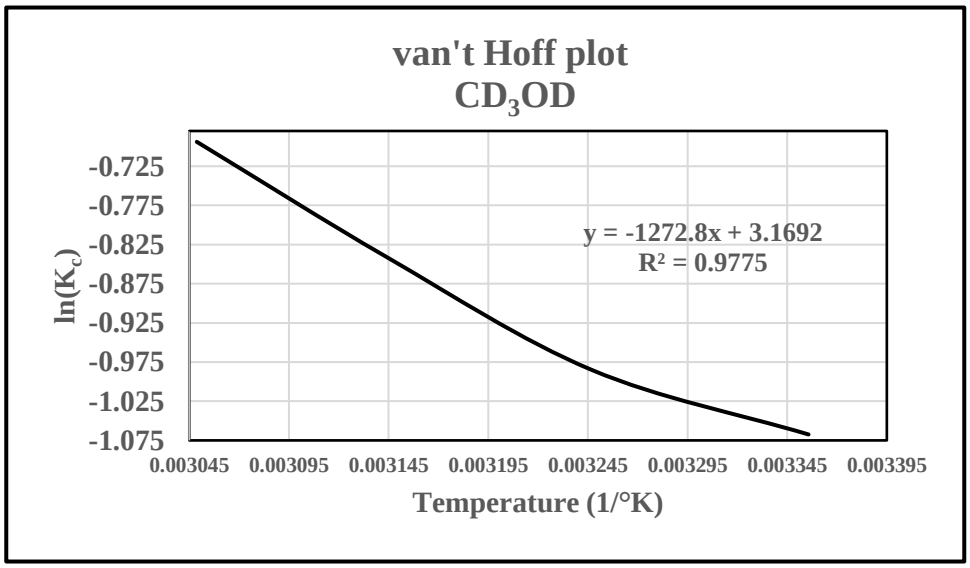


Figure 2 *van't Hoff plot for acetylacetone NMR plots in CD3OD*

From **Figure 1** and **Figure 2** the respective slopes and x-intercepts can be derived from the linear regressions as shown in the van't Hoff plots. Using **Equation 4**, **Equation 5**, and **Equation 6** the ΔH° and ΔS° are derived, for both solvent series.

$CDCl_3$:

$\Delta H° = -m * R$ = *(-)- 907.43 * 8.314463* = 7544.79

$\Delta S° = c * R$ = 10.6109 * 8.314463 = 10.61092

$\Delta G° = \Delta H° - \Delta S° * T$ = 2730.29

CD_3OD:

$\Delta H° = -m * R$ = (-)- 1272.8 * 8.314463 = 10582.65

$\Delta S° = c * R$ = 3.1692 * 8.314463 = 26.3502

$\Delta G° = \Delta H° - \Delta S° * T$ = 4382.74

Then comparing thermodynamic values by solvent, we get **Table 4** below:

Table 4 *Acetoacetone thermodynamic values*

Solvent	ΔH°	ΔS°	ΔG°
CD_3OD	10582.6	26.350	2730.29
$CDCl_3$	7544.8	10.611	4382.74

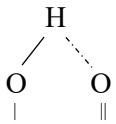
A single scan of ethyl acetoacetate in $CDCl_3$ at 25° C, was analyzed. It showed a K_c of 0.10 enol/keto, or 9.1% enol at equilibrium. With only one temperature scan, it was not possible to derive thermodynamic values from the equilibrium value. The H-NMR scan is shown in **Figure 4**, in the supplementary information, with the chemical shifts and integrations in **Table 6**, in the supplementary information.

3.2 Discussion

Acetylacetone will interconvert between its keto structure and its enol structure, as show below:

Acetylacetone

Ketone ⟷ Enol



$CH_3–CO–CH_2\text{-}CO\text{-}CH_3 \leftrightarrow CH_3–C{=}CH\text{-}C\text{-}CH_3$

Both structures are present when an H-NMR scan is performed on acetylacetone, with all distinct groups with hydrogens having signals. In the scans analyzed for this paper, the hydroxyl isn't within the scan width, so won't be discussed further. The first task is to correlate the hydrogen containing groups with the structural groups shown above.

The first thing to exam is the chemical shift of signals in a scan. Looking at **Figure 3**, in supplementary information, we see four signals plus the reference signal at the chemical shift of zero. In looking at the structure of the keto version, above, we see two methyl groups that are identical, with respect to the H-NMR scan, due to having an identical electronic environment, being this is a symmetric molecule and they are in the same position relative to the center. These six hydrogens will produce a single signal. This group is labeled 'd'. The methylene group in the center will produce a single signal as well. This group is labeled 'c'. These are all the hydrogen containing groups in the keto form.

For the enol structure, the simplistic structure commonly represented isn't accurate. It neglects internal hydrogen bonding, seen above. At first glance it would appear to have three non-identical hydrogen containing groups but given the fact the hydrogen and pi bonds will shift back and forth, the two methyl groups are electronically identical in an H-NMR scan. Both enol methyl groups are labeled 'e'.

The central CH is the last signal in this scan width, is labeled 'a'. Signals mentioned here are shown in **Figure 3**, with the labels mentioned here. This is the scan for acetylacetone in deuterated chloroform at 25° C. The methyl groups are adjacent to either a carbonyl or a hydroxyl, either of which can cause a chemical signal shift down-field, to a little higher ppm (approximately 0.7-1.3) than an alkane not adjacent to a carbonyl or a hydroxyl group. This corresponds to two signals seen in the scan, one at 2.0 and one at ~2.2 ppm. This seems to match the signals 'd' and 'e'.

The other two signals occur at 3.7 and 5.6 ppm. This seems to match what would be expected of a methylene between two carbonyls or a hydrogen on an SP^2 hybridized carbon adjacent to a carbonyl carbon. These fit best with groups labeled 'c' and 'a'. The signal at 5.6 ppm has a chemical shift expected of a hydrogen bonded via an SP^2 hybridized bond, which would identify it as group 'a'. The shift of 3.7 ppm is more expected of hydrogens on a carbon adjacent to carbonyl carbons which would correlate with group 'c'. In looking at the literature, this matches the correspondence of signals and groups in other experiments with acetylacetone. Below shows the signal label and structure matching. [11]

When looking at the signal multiplets, all are singlets as expected, given no group is adjacent to a carbon with attached hydrogen(s), preventing any spin-coupling. As a sanity check, the integration value of 'd' divided by that of 'c' yields about 2.83, close enough to the expect 3 (or 6 / 2) to make sense. Similarly, dividing the integration values of 'e'/'a' yields 6.2 which again is in the close neighborhood of 6 (or 6 / 1). The integration values for acetylacetone in both solvents can be found in **Table 5**, in the supplementary information.

To compare the keto and enol integration values, to get the relative proportion of each, either ‘c’/’a’ or ‘d’/’e’ would work. That said, ‘d’ and ‘e’ have the advantage of being stronger signals and not needing to correct for a different number of hydrogens. When comparing the integration value of the group ‘d’ (keto) to the group ‘e’ (enol) we get:

Equation 7 *Keto/Enol equilibrium constant Kc*

$$K_c = d_{int} / e_{int}$$

For the $CDCl_3$ solvent equilibrium @ 25° C we get

$$K_c = 0.17 / 1.00 = 0.17, \quad \text{or a ratio of 0.17:1.00 keto to enol}$$

For the CD_3OD solvent equilibrium @ 25° C we get

$$K_c = 0.34 / 1.00 = 0.34, \quad \text{or a ratio of 0.34:1.00 keto to enol}$$

The other equilibrium constants, at the different temperatures are found in **Table 5**, in the supplementary information.

In comparing the set of equilibrium constants at the four different temperatures (25, 35, 45, 55° C), utilizing a van’t Hoff plot, values for standard enthalpy, entropy, and Gibbs Free energy can be derived, as shown earlier in **Table 4**. In looking at the values in that table we see that in deuterated methanol, acetylacetone has a higher standard enthalpy and entropy than in deuterated chloroform. The equilibrium is shifted significantly to the enol side of the equation in the chloroform solvent. Methanol is more polar than chloroform but is also protic, which introduces intermolecular hydrogen bonding not occurring in chloroform. Given the intramolecular hydrogen bonding is what is stabilizing the enol form, the intermolecular hydrogen bonding would interfere with that stability. This can be seen in the ~10% lower concentration of the enol form in the methanol solvent. Additionally, the lower heat of enthalpy in the chloroform solvent shows the enol form is more stabilized.

As seen in **Table 5, Figure 1, and Figure 2,** the rate of change in K_c, shifting toward the keto side, is more pronounced in methanol than chloroform. The general trend toward less enol can be seen as the disruption of the intramolecular hydrogen bonding stabilizing the enol form. As it becomes less stable the keto form increases in percent and the K_c drops. In the methanol solvent, with the higher heat of enthalpy, adding energy is going to push the equilibrium to the left (toward keto form) faster than with chloroform, in agreement with Le Chatelier's principle.

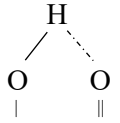
In examining the structure of ethyl acetoacetate an ethyl group is present in both keto and enol forms. On

the H-NMR the ethyl will show two signals, one for the terminal methyl group and one for the methylene group. This is due to both the enol and the keto structures having an electronic environment that is virtually identical, such that the CH_2 only has one signal and the CH_3 only has one signal, for both the enol and keto structures. These methylene and methyl groups are labeled ‘b’ and ‘f’, respectively. The methyl group, ‘f’, is fairly distant from the deshielding effects of the carboxyl group, so its chemical shift is up field, in the neighborhood of 0.7 to 1.3, typical of an alkane. On the scan, a triplet (n+1) was found at 1.25 ppm. A methyl adjacent to a methylene group would normally expect to produce this type signal, due to the spin-coupling of the adjacent two hydrogens.

The methylene group is expected to be a quartet (n+3) due to having three hydrogen neighbors, and no other adjacent hydrogens. Considering it’s the proximal end of an ethyl group as part of an ester, a chemical shift of between 3.4 and 4.8 ppm would be expected. A quartet signal was found at 3.9 ppm, and is the only quartet in the scan, so this correspondence makes sense. This signal and group were labeled ‘b’. The enol CH group should produce a singlet (n+0) due to zero neighboring hydrogens. Due to its SP^2, alkenyl hydrogen nature, it would be expected in the range of 4.5 to 6.8 ppm. A singlet was found at 5.0 ppm, which fits this CH hydrogen. It was labeled ‘a’. The coupling constant between the ‘b’ and ‘f’ groups is virtually the same.

The methylene of the keto should be a singlet, given no neighboring hydrogens, and moderately down field due to the two neighboring carbonyls. A range of 2 – 3 ppm is expected for hydrogen adjacent to a carbonyl, so neighboring two might shift it a little more down field. A singlet was discovered at 3.5 ppm, which seems to fit that methylene group. It was labeled ‘c’.

There are two methyl groups, each at the left of the structures (enol and keto) above. Given they are electronically unique, they should show different signals/chemical shifts. Both are expected to be singlets, given no neighboring hydrogens to spin-couple with. Assigning these to enol or keto, solely on the chemical shift would be difficult given the non-identical but similar electronic environment, so additional information will be needed. Looking at groups labeled ‘a’ and ‘c’, which were the same positional carbon on the respective enol and keto forms, if the ‘c’ integration value is halved, scaling for twice the number of hydrogens, then the ‘c’/’a’ value is approximately ten. This shows the keto form should be in predominance, at equilibrium in this solvent, at 25° C. The two methyl groups previously mentioned have the same number of hydrogens, so no scaling is needed to compare them. In comparing the two methyl integrals, ‘e’/’d’ yields a value of exactly ten. This shows ‘e’ is the keto methyl and ‘d’ is the enol methyl.



CH_3–CO–CH_2-COO-CH_2-CH_3 ←→ CH_3–C=CH-C-O-CH_2-CH_3

Groups e c b f d a b f

Using the previously mentioned integral values, the enol/keto K_c is 0.10, or about 0.09% enol. With the equilibrium so strongly shifted to the keto form, when compared to the acetylacetone equilibria, one can conclude the keto form is a much more stable form for ethyl acetoacetate. The carboxyl group of the ester seems to destabilize the intramolecular hydrogen bonding that was key to stabilizing the enol form in acetylacetone. There is also the stability of the acetylacetone having two resonance enol forms, with the ester group of ethyl acetoacetate not having.

Given there one only one ethyl acetoacetate scan available, no thermodynamic values could be computed.

4.0 CONCLUSIONS

Two, four scan sets of solvated acetylacetone, one in CDCl3 and another in CD_3OD, were analyzed from provided FID data files. For each set, there was an FID for scans at 25, 35, 45, and 55° C. A single FID was furnished for ethyl acetoacetate in deuterated chloroform run at 25° C. The files were processed, mappings of groups to signals made, and the data derived and compiled. The equilibriums were computed for the acetoacetone data, for both solvations, with the CD_3OD solvated acetylacetone having K_cs from 2.97 – 2.00 and the $CDCl_3$ solvated scans with K_cs from 5.88-4.35. The regressions performed on van't Hoff plots of the $\ln(K_c)$ versus inverse temperature (1/K°). The linear regressions of the plots produced $y = -907.43x + 1.2762$ for the $CDCl_3$ scans and $y = -1272.8x + 3.1692$ for the CD_3OD scans. Thermodynamic values were computed from this information for both solvent sets. The $CDCl_3$ solvated scans showed a standard enthalpy of 7.545 kJ/mol, an entropy of 10.61 J/mol-K, and a Gibbs Free energy of 2.730 kJ/mol. The CD_3OD solvated scans showed a standard enthalpy of 10.583 kJ/mol, an entropy of 26.350 J/mol-K, and a Gibbs Free energy of 4.383 kJ/mol.

From the equations above, for both solvation sets of acetylacetone scans, there is a shift toward the keto form as the temperature rose, due an increase in entropy and to interference with the intramolecular hydrogen bonding stabilizing acetylacetone's enol form. The enol concentration was smaller in the deuterated methanol than for the deuterated chloroform, despite the latter's lower polarity. This is thought to be due to the interference with intramolecular hydrogen bonding by the competing intermolecular hydrogen bonding of the protic solvent, stabilizing the carbonyl thus reducing the change to the enol hydroxyl. Ethyl acetoacetate showed a sharply diminished enol-keto equilibrium, compared to acetylacetone, due to the carboxyl ester in the molecule. Its K_c was 0.10.

Some key points of this research are: acetylacetone has an equilibrium strongly weighted to the enol form; that protic, polar solvents can interfere with this shift compared to polar aprotic solvents; and the equilibrium starts shifting back to the keto form with increasing temperatures. It was shown that other β-dicarbonyls, like ethyl acetoacetate, have an equilibrium farther to the keto form ($K_c < 1$) and closer to the simpler carbonyls.

5.0 REFERENCES

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6.0 SUPPLEMENTAL INFORMATION

6.1 Significant Figures

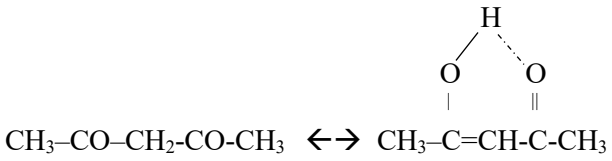
Significant figures used were the significant figures of the raw data plus one, for all calculation results.

6.2 Raw Data

Available on request.

6.3 Tables, Graphs, and Plots

Acetylacetone in $CDCl_3$ @ 25°C



Groups d a d e c e

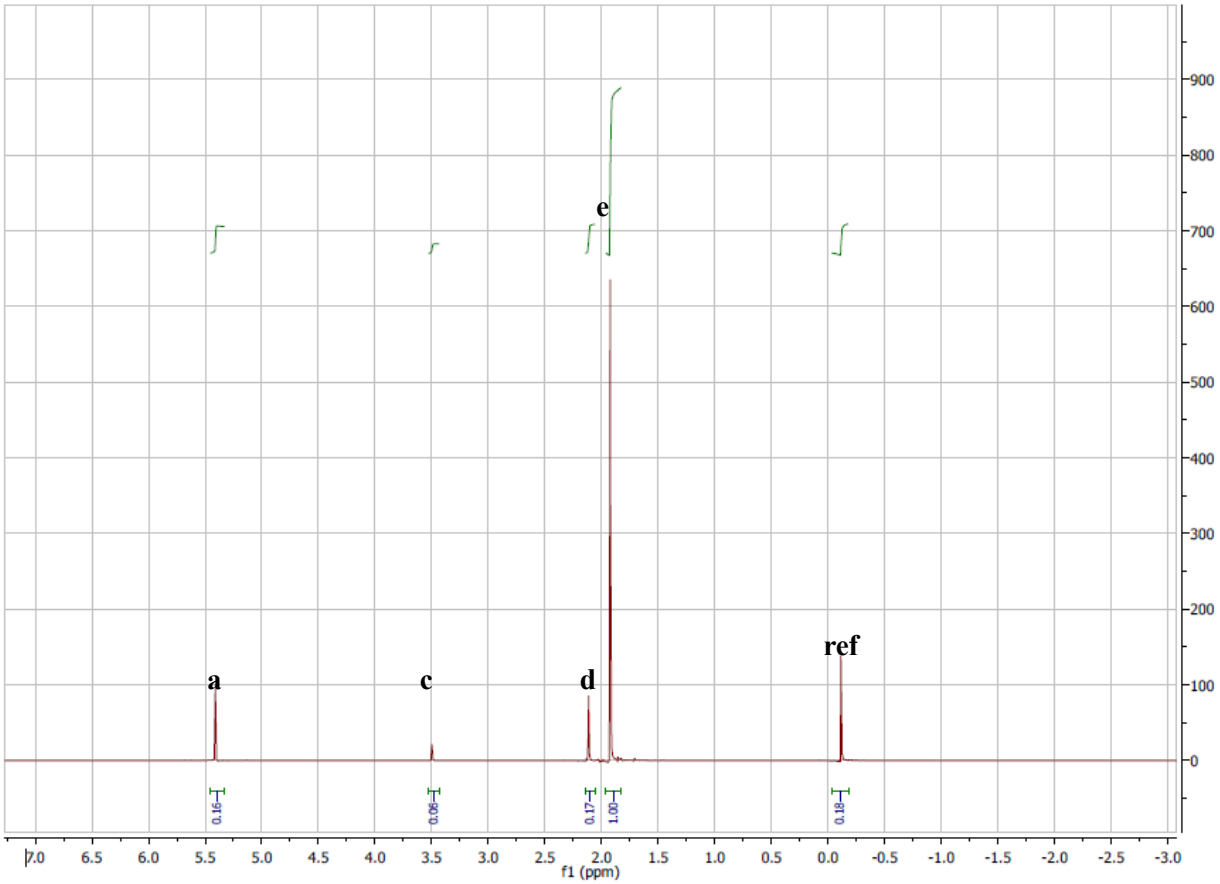


Figure 3 *Acetylacetone scan in CDCl3 at 25° C*

Acetylacetone in CD_3OD @ 25° C

$CH_3–CO–CH_2\text{-}C\text{-}CH_3 \leftrightarrow CH_3–C{=}CH\text{-}C\text{-}CH_3$

Groups d a d e c e

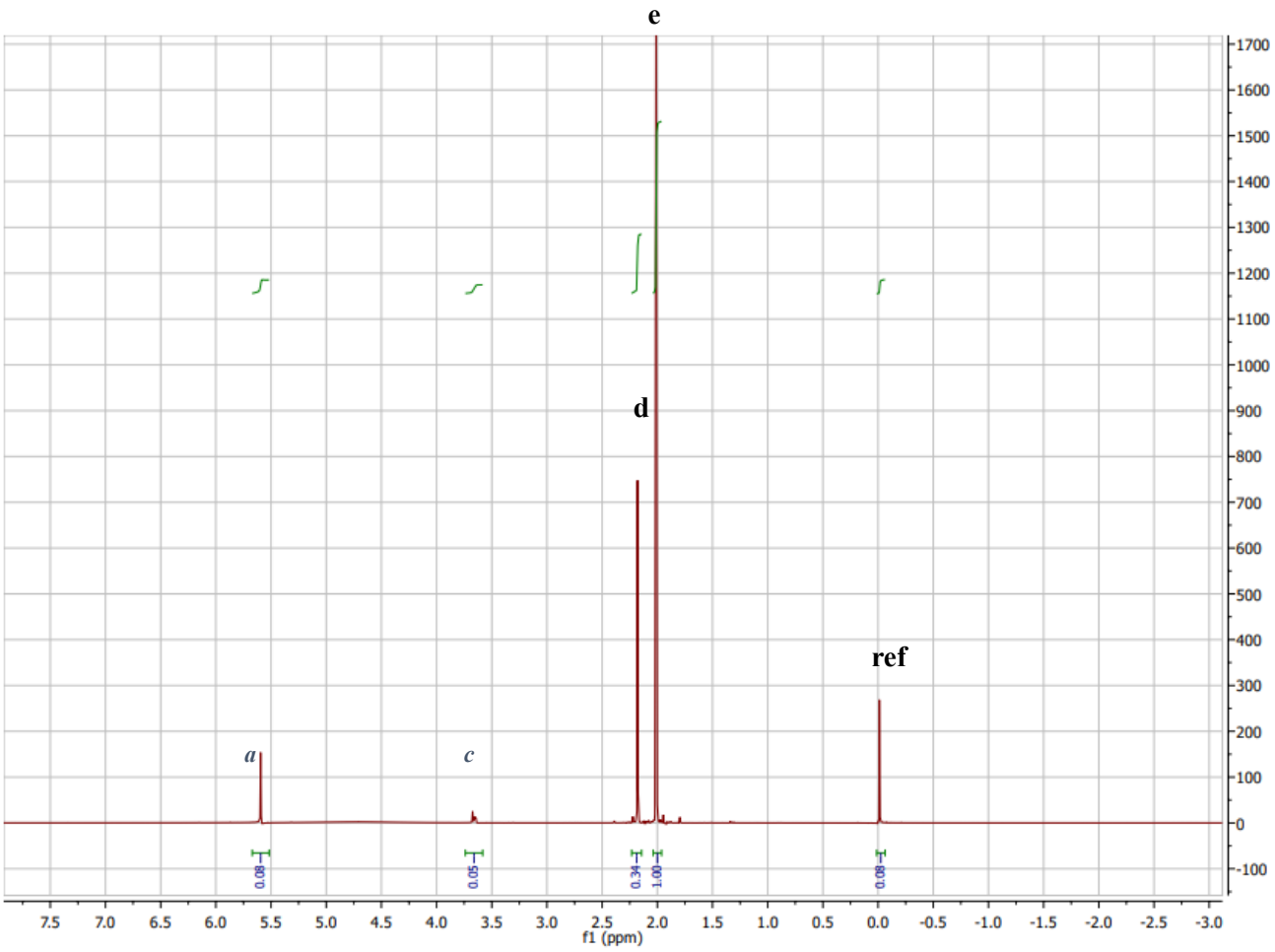


Figure 4 *Acetylacetone scan in CD_3OD at 25° C*

Ethyl acetoacetate in $CDCl_3$ @ 25°C

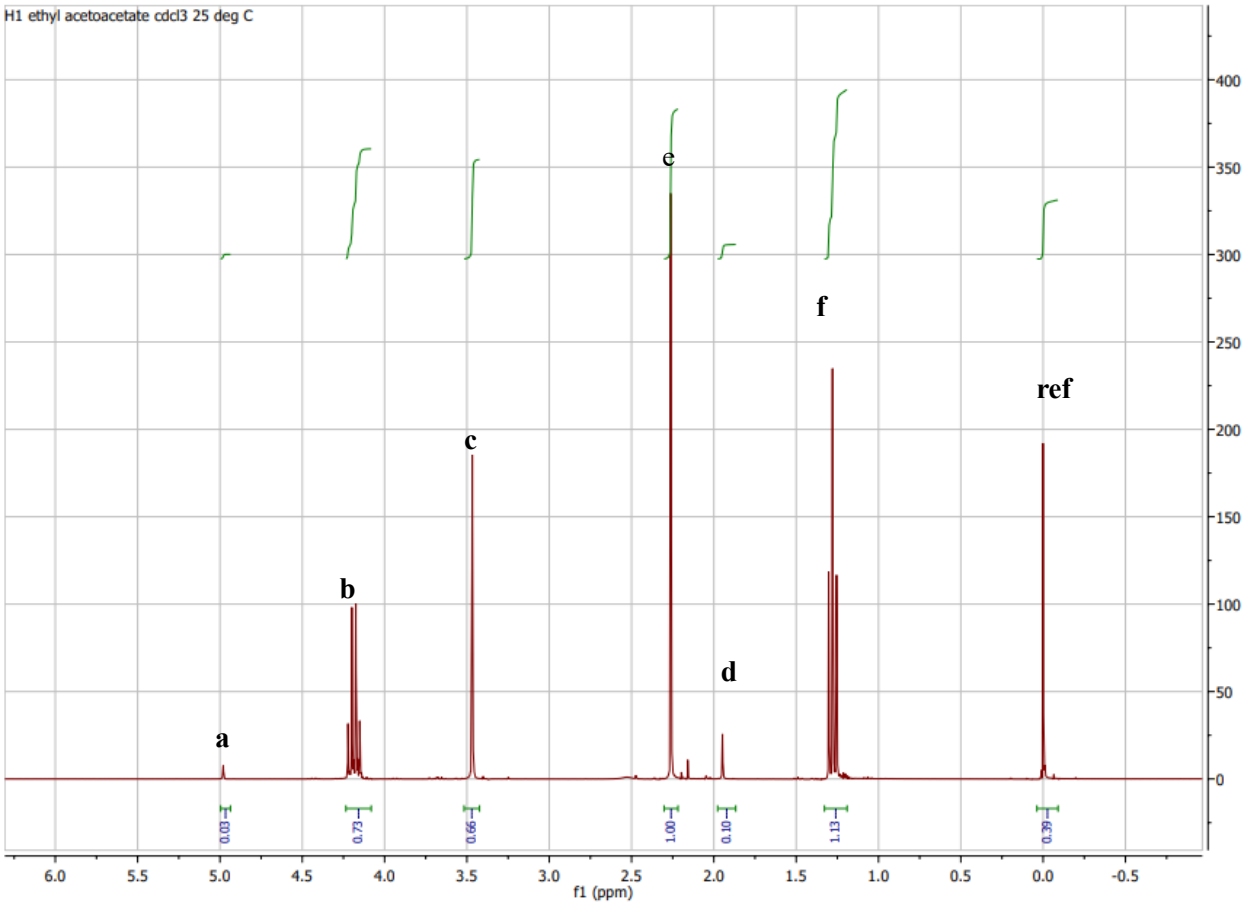


Figure 5 *Ethyl acetoacetate in $CDCl_3$ @ 25°C*

Table 5 *Consolidated table of H-NMR data for acetylacetone scans*

acetylacetone $CH_3–CO–CH_2-CO-CH_3 \longleftrightarrow CH_3–COH=CH-CO-CH_3$										
	Groups	d	c	d	e	a	e			
CD_3OD						$CDCl_3$				
Index	Group	Range	Intensity Normalized	Integration Absolute		Index	Group	Range	Intensity Normalized	Integration Absolute
@25°		K_c = ratio e/d =	2.94	75% enol		@25°		K_c = ratio e/d =	5.88	86% enol
1	a	5.67 .. 5.52	0.08	1884.2		1	a	5.45 .. 5.33	0.16	1294.2
2	c	3.74 .. 3.58	0.05	1200.3		2	c	3.53 .. 3.44	0.06	446.6
3	d	2.23 .. 2.14	0.34	8239.8		3	d	2.14 .. 2.06	0.17	1393.9
4	e	2.04 .. 1.96	1.00	23960.9		4	e	1.96 .. 1.83	1.00	8060.8
5	Ref	0.01..-0.06	0.08	1920.7		5	Ref	-0.03..-0.18	0.18	1416.1
@35°		K_c = ratio e/d =	2.70	73% enol		@35°		K_c = ratio e/d =	5.26	84% enol
1	a	5.63 .. 5.54	0.07	1650.0		1	a	5.43 .. 5.38	0.16	1233.1
2	c	3.71 .. 3.52	0.06	1281.8		2	c	3.50 .. 3.44	0.06	457.9
3	d	2.21 .. 2.14	0.37	8441.4		3	d	2.15 .. 2.07	0.19	1431.7
4	e	2.06 .. 1.97	1.00	22601.7		4	e	1.93 .. 1.89	1.00	7592.4
5	Ref	-0.01..-0.13	0.09	1953.9		5	Ref	-0.08..-0.15	0.19	1437.6
@45°		K_c = ratio e/d =	2.32	70% enol		@45°		K_c = ratio e/d =	5.00	83% enol
1	a	5.65 .. 5.53	0.08	1642		1	a	5.46 .. 5.31	0.16	1214.4
2	c	3.70 .. 3.58	0.06	1269		2	c	3.52 .. 3.42	0.07	502.6
3	d	2.25 .. 2.08	0.43	9245		3	d	2.14 .. 2.05	0.20	1510.5
4	e	2.06 .. 1.91	1.00	21455		4	e	1.94 .. 1.83	1.00	7672.0
5	Ref	-0.01..-0.08	0.08	1823		5	Ref	0.01..-0.19	0.18	1412.3
@55°		K_c = ratio e/d =	2.00	67% enol		@55°		K_c = ratio e/d =	4.35	81% enol
1	a	5.63 .. 5.46	0.07	1426.6		1	a	5.47 .. 5.33	0.16	1181.8
2	c	3.69 .. 3.60	0.07	1296.9		2	c	3.54 .. 3.43	0.07	533.9
3	d	2.23 .. 2.11	0.50	9689.1		3	d	2.17 .. 2.05	0.23	1668.8
4	e	2.04 .. 1.92	1.00	19392.1		4	e	1.97 .. 1.80	1.00	7171.4
5	Ref	0.07..-0.12	0.10	1856.9		5	Ref	-0.00..-0.19	0.19	1365.4

Table 6 *H-NMR data of ethyl acetoacetate in CDCl3 @25°, Kc = 0.10, 9.1% enol*

Index	Group	Range	Normalized	Absolute
1	a	5.00 .. 4.94	0.03	118.53
2	b	4.23 .. 4.08	0.73	2931.08
3	c	3.52 .. 3.42	0.66	2647.01
4	e	2.30 .. 2.22	1.00	3992.10
5	d	1.98 .. 1.87	0.10	383.88
6	f	1.33 .. 1.19	1.13	4504.34
7	Ref	0.04 .. -0.09	0.39	1566.62