Intramolecular Hydrogen Bonding (Proton Transfer) of 1-Phenyl-1,3-butanedione

Hideyo Matsuzawa*, Takashi Nakagaki and Makio Iwahashi
School of Science, Kitasato University (1-15-1 Kitasato, Sagamihara, Kanagawa-ken, 228-8555 JAPAN)

Abstract: Through the $^1$H and $^{13}$C NMR measurements for the symmetrical $\beta$-diketones such as 2,4-pentanedione and 1,3-diphenyl-1,3-propanedione and unsymmetrical one such as 1-phenyl-1,3-butanedione at various concentrations and temperatures, we confirmed that 1-phenyl-1,3-butanedione in CDCl$_3$ exists as monomers in its relatively low concentration. In addition, the 1-phenyl-1,3-butanedione in CDCl$_3$ exists not as a keto-form but as two kinds of cis-enol forms. The proton transfer between the two kinds of cis-enols for 1-phenyl-1,3-butanedione was discussed thermodynamically; it is concluded that the OH proton of enol of 1-phenyl-1,3-butanedione is considerably located near the oxygen atom attached to the carbon atom linking to a phenyl group.

Key words: hydrogen bonding, proton transfer, $^1$H and $^{13}$C NMR $\beta$-diketone, 1-phenyl-1,3-butanedione, 2,4-pentadione, 1,3-diphenyl-1,3-propanedione

1 INTRODUCTION

Proton having a small mass and radius shows various characteristic phenomena such as hydrogen bonding and tunneling effect. The tunneling effect is significantly related to the proton transfers, which are very important for the chemical and biological aspects. Many investigations concerning proton transfers have been carried out[1-5]. For example, the proton transfer between two molecules of dimeric benzoic acid is so rapid that it can not be observed at room temperature[6]. The proton transfer is able to be observed only at very low temperature[6]. This is because the activation energy of the proton transfer is extremely low.

By the way, $\beta$-diketone generally exists as cis-enol form in solid state and as the mixture of diketo and cis-enol forms in its liquid and gaseous states; its trans-enol form is not observed[7]. Therefore, in the liquid state of $\beta$-diketone its diketo form is thought to be in equilibrium with its cis-enol form. However, $\beta$-diketone having a large functional group such as phenyl or thiophenyl group in solvents is apt to take almost 100% of cis-enol form[8-10].

With respect to the cis-enol forms of $\beta$-diketone, several phenomena suggesting a proton transfer between the two enol forms (a- and b-forms) as represented in Fig. 1 have been reported[11-15]. However, the phenomena have been also explained by the existence of the resonance structure, c, shown in Fig. 1[16-19]. For the case of the two enol forms (a and b), there should be two minima in the potential surface for $\beta$-diketone and for the case of the resonance structure c, there should be only one minimum.

The $\beta$-diketone having the two cis-enol forms, whose functional groups X and Y represented in Fig. 1 are extremely different (unsymmetrical) from each other, probably exhibits a relatively slow proton transfer observable by ordinary methods and at ordinary temperatures. If we observe the proton transfer by ordinary methods and at ordinary temperatures, we can know more exactly what determines such the phenomena.

In the present study, we measured the $^1$H and $^{13}$C NMR chemical shifts for the symmetrical $\beta$-diketones such as 2,4-pentanedione ($X = CH_3$, $Y = CH_3$) and 1,3-diphenyl-1,3-propanedione ($X = phenyl$, $Y = phenyl$) and unsymmetrical one such as 1-phenyl-1,3-butanedione ($X = phenyl$, $Y = CH_3$) to confirm the existence of the enol form and the equilibrium state of proton transfer between two kinds of enol forms for unsymmetrical $\beta$-diketone.

*Correspondence to: Hideyo Matsuzawa, School of Science, Kitasato University, 1-15-1 Kitasato, Sagamihara, Kanagawa-ken, 228-8555 JAPAN
E-mail: matsu@sci.kitasato-u.ac.jp
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2 EXPERIMENTAL

2.1 Samples
Samples of 1-phenyl-1,3-butanedione and 1,3-diphenyl-1,3-propanedione (Kantoh Chemical Co. Ltd., purity > 99.8\%) were purified through twice recrystallizations from diethyl ether. Sample of 2,4-pentanedione (Junsei Chemicals, purity > 99\%) was distilled for purification under a reduced pressure. Acetone (Wako Junyaku Co. Ltd., purity > 99.0\%) was distilled for purification. CDCl$_3$ (Merck, purity > 99.8\%) and HCl (Wako Junyaku Co. Ltd., the most pure grade) were used without further purification for the NMR measurements.

2.2 NMR measurements
$^1$H and $^{13}$C NMR measurements were carried out on an NMR spectrometer (Japan Electron Optics Laboratory (JEOL) Model EX-400). All the measurements were made on protons at 399.65 MHz and on $^{13}$C nuclei at 100.40 MHz, respectively. Proton noise decoupling technique was employed for $^{13}$C NMR measurement. For the NMR measurements in CDCl$_3$, tetramethylsilane (TMS) dissolved in CDCl$_3$ was enclosed in an inner tube, and it was used as a standard.

3 RESULTS AND DISCUSSION

3.1 $^1$H NMR spectrum
Figure 2 shows the $^1$H NMR spectrum for the $4 \times 10^{-3}$ mol dm$^{-3}$ sample of 1-phenyl-1,3-butanedione (unsymmetrical $\beta$-diketone) in CDCl$_3$ at 27.5°C. Two signals assigned to C$_3$ and C$_1$ atoms exist at 193.714 and 185.355 ppm, respectively. This signal assignments for the C$_1$ and C$_3$ atoms were carried out by comparing with the two single signals at 185.759 and 191.154 ppm in the spectra for 1,3-diphenyl-1,3-propanedione ($^\alpha$H) and 2,4-pentanedione ($^\alpha$H), respectively.

In $^\alpha$H, in addition, there are more signals: signals due to the carbon atoms of phenyl group exist between 134.929 and 127.010 ppm; a signal due to the C$_2$ atom, at 96.707 ppm; three signals due to the C atom of CDCl$_3$, at 77.377, 77.000 and 76.736 ppm; a signal due to the C atom of CH$_3$, at 25.823 ppm.

As mentioned above, in the case of the symmetrical $\beta$-diketones such as 1,3-diphenyl-1,3-propanedione and 2,4-pentanedione, the signals for C$_3$ and C$_1$ atoms became only one sharp signal. This also suggests that unsymmetrical 1-phenyl-1,3-butanedione exists in the two $cis$-enol forms.

Next, we observed temperature dependence of the $^{13}$C NMR chemical shift of 1-phenyl-1,3-butanedione. The con-
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Signals of C3 atom shifted to higher magnetic field direction with increasing temperature, whereas that of C1 atom shifted to lower one, whereas other signals remained almost constant. The changes in the chemical shifts for C1 and C3 atoms with increasing temperature mean that 1-phenyl-1,3-butanedione does not take the resonance structure D. This is because the chemical shift of C atom in the resonance structure should not be altered with temperature, since the electron density in the resonance ring of β-diketone molecule does not change with temperature. Shapet’ko also denied the existence of the resonance structure by the fact that the 1H NMR chemical shifts for β-carbonyl compounds were not observed with the change in temperature18).

In addition, the change in the chemical shifts for C1 and C3 atoms with increasing temperature means that, for the cis-enol form of 1-phenyl-1,3-butanedione, an intramolecular proton transfer occurs very quickly beyond the detection ability of NMR: The chemical shifts of C1 and C3 produced by the temperature changing are thought to result from the change in the content ratio of a- to b-form enols (Fig. 1).

To determine the content ratio of a- to b-form enols we calculated the equilibrium constant, K, between a- and b-forms of 1-phenyl-1,3-butanedione from the chemical shift of C3 atom at various constant temperatures. The relationship between the chemical shift and K is expressed as:19)

\[ K = \frac{[b]}{[a]} = \frac{\tau_b}{\tau_a} \]

where \([a]\) and \([b]\) are concentrations of a- and b-forms, respectively; \(\tau_a\) and \(\tau_b\) are individual residence time of OH proton at the positions of a- and b-forms.

The chemical shift (\(\delta_{XY}\), ppm) for the \(i\)-th carbon atom (C) for unsymmetrical β-diketone (X ≠ Y) taking two kinds of enol forms is the weight-average chemical shifts of the carbon atoms in the a- and b-forms\(^{20}\).

Thus,

\[ \delta_{XY} = \frac{\delta_a \tau_a + \delta_b \tau_b}{\tau_a + \tau_b} = \frac{\delta_a + \delta_b K}{1 + K} \]

where \(\delta_a\) and \(\delta_b\) are the chemical shifts for a complete a- and b-forms, respectively.

When \(X = Y\), \([a]\) equals \([b]\) and then \(K = 1\).

Thus,
\[ \delta_{XX} = \frac{\delta_a + \delta_b}{2} \]  

(3)

From the equation 3, we obtain

\[ \delta_b = 2\delta_{XX} - \delta_a \]  

(4)

Consequently, from the chemical shift for a carbon atom of symmetrical \( \beta \)-diketone \((X=Y)\) in its enol form and the one chemical shift, \( \delta_a \), for a carbon atom existing at completely localized position of a-form, we can estimate the other one, \( \delta_b \), at completely localized position of b-form.

Next, from the equation 2, we obtain equation 5:

\[ K = \frac{\delta_a - \delta_{XY}}{\delta_{XY} - \delta_b} \]  

(5)

If we know the value of \( \delta_a \), we can estimate the value of \( \delta_b \) by using the equation 4 and then \( K \) by using the equation 5.

Now let note the chemical shifts of \( C_3 \) atom for determining the \( K \) value for the equilibrium between a- and b-forms of 1-phenyl-1,3-butanedione \((X=\text{Phenyl and } Y=\text{CH}_3)\). First of all, to obtain the \( \delta_{XX} \) value we used 2,4-pentanedione \((X=Y=\text{CH}_3)\), which has a close value of the chemical shift of \( C_3 \) atom to that of 1-phenyl-1,3-butanedione. Secondly, for the estimation of \( \delta_a \), i.e., the chemical shift of \( C_3 \) atom for the complete a-form of 2,4-pentanedione, we used the value of the chemical shift of carbon atom of methylvinylketone\(^{20}\). Furthermore, for the correlation of the effect of the hydrogen bonding between proton and oxygen atom of carbonyl group on the chemical shift of \( C_3 \) atom, we used a difference value between the chemical shift of carbon atom for acetone and that for acetone containing small amount of HCl. The reason why we used acetone instead of methylvinylketone is that the latter is apt to be polymerized with the aid of HCl.

Table 1 shows the chemical shift values for \( C_3 \) atom of three kinds of samples and the hydrogen bonding correlation terms at various temperatures. In the determination of the temperature dependence of the chemical shift of \( C_3 \) atom for various samples, we used the signal \((77.0 \text{ ppm})\) for the carbon atom of CDCl\(_3\) as a standard instead of TMS since the 77.0 ppm signal was always constant irrespective of the concentration of sample and temperature. The chemical shift for each sample shifts toward lower magnetic field direction with increasing temperature.

Now let estimate the \( K \) value for the equilibrium between a- and b-forms of 1-phenyl-1,3-butanedione at 27.5°C as a typical example.

Inserting 199.851 ppm as \( \delta_a (= 199.840 + 0.011) \): chemical shift of carbon atom of methylvinylketone + the correlation term to the hydrogen bonding effect) and 191.154 ppm as \( \delta_{XX} \) (chemical shift of \( C_3 \) carbon of 2,4-pentadione) into the equation 4 gives 182.457 ppm as \( \delta_b \). In addition, inserting 193.714 ppm as \( \delta_{XY} \) (chemical shift of \( C_3 \) carbon atom of 1-phenyl-1,3-butanedione) and the obtained values of \( \delta_a \) and \( \delta_b \) in the equation 5 gives \( K = 0.545 \). Thus, the content ratio of a-form to b-form is 1.83 : 1. Namely, the proton of the cis-enol is almost twice located near the oxygen atom attached to the carbon atom linking to a phenyl group (a-form enol). Gordetsky et al., obtained \( K = 0.775 \) from the \(^{17}\text{O}\) NMR observations\(^{21}\). Their results also support that the proton is mainly located near the oxygen atom attaching to \( C_1 \) atom linking to a phenyl group.

The \( K \) values for 1-phenyl-1,3-butanedione at various temperatures are tabulated in Table 2. The \( K \) value increases with increasing temperature: The proton located near the oxygen atom attaching to \( C_1 \) atom linking to a phenyl group is apt to more transfer to the oxygen atom attaching \( C_3 \) atom linking to a methyl group with increasing temperature.

Figure 6 shows the van’t Hoff plots of the \( K \) values. A relatively good straight line is obtained. From the inclination of the line, we obtained 347 J mol\(^{-1}\) as the transformation enthalpy from a-form enol to b-form one. Namely, 1-phenyl-1,3-butanedione which exists cis-enol form in the concen-

<table>
<thead>
<tr>
<th>Samples</th>
<th>Temperature / °C</th>
<th>Chemical Shift / ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-phenyl-1,3-butanedione</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- 43.5</td>
<td>194.244</td>
<td></td>
</tr>
<tr>
<td>- 20.5</td>
<td>194.079</td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>193.915</td>
<td></td>
</tr>
<tr>
<td>27.5</td>
<td>193.714</td>
<td></td>
</tr>
<tr>
<td>2,4-pentanedione</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- 43.5</td>
<td>191.483</td>
<td></td>
</tr>
<tr>
<td>- 20.5</td>
<td>191.374</td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>191.282</td>
<td></td>
</tr>
<tr>
<td>27.5</td>
<td>191.154</td>
<td></td>
</tr>
<tr>
<td>methylvinylketone</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- 43.5</td>
<td>200.340</td>
<td></td>
</tr>
<tr>
<td>- 20.5</td>
<td>200.120</td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>199.990</td>
<td></td>
</tr>
<tr>
<td>27.5</td>
<td>199.840</td>
<td></td>
</tr>
<tr>
<td>Correlation term of hydrogen bonding</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- 43.5</td>
<td>+0.037</td>
<td></td>
</tr>
<tr>
<td>- 20.5</td>
<td>+0.037</td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>+0.055</td>
<td></td>
</tr>
<tr>
<td>27.5</td>
<td>+0.011</td>
<td></td>
</tr>
</tbody>
</table>

\( \text{Table 1 Chemical Shifts of } C_3 \text{ Carbon Atom of Various Ketones.} \)
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4 CONCLUSION

It is concluded that 1-phenyl-1,3-butanedione in CDCl$_3$ exists as not diketone form but cis-enol form monomers through $^1$H and $^{13}$C NMR measurements. Through the $^{13}$C NMR chemical shift measurements for the symmetrical 2,4-pentanedione and 1,3-diphenyl-1,3-propanedione and unsymmetrical 1-phenyl-1,3-butanedione we have clarified that 1-phenyl-1,3-butanedione in CDCl$_3$ exists as two kinds of cis-enol forms. The chemical shift of C$_3$ carbon atom attributes to the proton transfer between the two kinds of cis-enols for 1-phenyl-1,3-butanedione; from the thermodynamic discussion for the proton transfer it is concluded that the OH proton of enol of 1-phenyl-1,3-butanedione is considerably located near the oxygen atom attached to the carbon atom linking to a phenyl group.

Table 2  Equilibrium Constant, $K$, between a- and b-form Enols of 1-phenyl-1,3-butanedione at Various Temperatures.

<table>
<thead>
<tr>
<th>Temperature / °C</th>
<th>Equilibrium constant, $K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-43.5</td>
<td>0.526</td>
</tr>
<tr>
<td>-20.5</td>
<td>0.529</td>
</tr>
<tr>
<td>1.5</td>
<td>0.538</td>
</tr>
<tr>
<td>27.5</td>
<td>0.545</td>
</tr>
</tbody>
</table>

Fig. 6  Van’t Hoff Plots for the Equilibrium Constant $K$ between a- and b-form Enols of 1-phenyl-1,3-butanedione.

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References

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