Optical studies on the effect of pressure IV: the effects of pressure on the keto-enol equilibria of ethyl acetoacetate and acetylacetone

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OPTICAL STUDIES ON THE EFFECT OF PRESSURE IV
The Effects of Pressure on the Keto-Enol Equilibria of Ethyl Acetoacetate and Acetylacetone

By JIRO OSUGI, TETSUO MIZUKAMI and TADAFUMI TACHIBANA

The effects of pressure on the keto-enol equilibria of ethyl acetoacetate and acetylacetone in the solvents of methanol, ethanol, iso-propanol, n-hexane and n-heptane have been studied from the measurement of the ultraviolet spectra at high pressure.

Comparing the molal volume of the keto form with that of the enol form, which are conjectured from their parachors, it is expected that the enol form is favorable with increasing pressure.

However, the effect of pressure on the keto-enol equilibria of ethyl acetoacetate and acetylacetone is small. The keto-enol equilibria of ethyl acetoacetate and acetylacetone shift to the keto form in the polar solvents, and to the enol form in the non-polar solvents at high pressure.

From these results, it is expected that the variation of the dielectric constant of the solvent with pressure would have influence upon the keto-enol equilibria at high pressure. That is, it may be necessary to consider the following factors for the purpose of studying the effects of pressure on the keto-enol equilibria.

I The volume change of tautomers.
II The increment of the dielectric constant of the solvent with increasing pressure.

Introduction

As for the studies on the keto-enol equilibria, in order to determine the concentration of the enol form, the titration method\(^1\), the molecular refraction\(^2\), the ultraviolet spectrum\(^3\), the infrared spectrum\(^4\) and the nuclear magnetic resonance spectroscopy\(^5\) have been used.

The effect of pressure on the keto-enol equilibria of ethyl acetoacetate in various solvents and the pure ester were studied by Kabachnik et al\(^6\), and Le Noble\(^7\), respectively. However, they determined the concentration of the enol form by the titration method after releasing pressure. Kabachnik et al. reported that the effect of pressure varied with solvent. Some studies on the keto-enol equilibria were carried out by the ultraviolet spectrum, since Grossmann did\(^8\).

(Received February 3, 1967)

1) K. H. Meyer and F. Kappelmeier, Ber., 44, 2718 (1911)
5) J. L. Burdett and M. T. Rogers, J. Am. Chem. Soc., 86, 2105 (1964)
8) P. Grossmann, Z. physik. Chem., 109, 305 (1924)
This paper reports the results obtained from the studies on the effects of pressure on the keto-enol equilibria of ethyl acetoacetate and acetylacetone in various solvents by the measurements of the ultraviolet spectra at high pressure.

**Experimental**

Ethyl acetoacetate and acetylacetone, and methanol, ethanol, iso-propanol, n-hexane and n-heptane, commercially offered as guaranteed reagents, treated with the ordinary purification method, were used as the samples and solvents, respectively.

These solvents were chosen from the view of the following criteria.
1. No absorption band in the experimental range of wave length.
2. No solidification under the experimental pressure.
3. No reactivity with the carbonyl group.
4. No corrosive action to the optical vessel.

The optical vessel with sapphire windows is the same as reported in the previous paper9). The photoelectric photometer used is Hitachi EPU-2 A. The dots of spectra at the interval of 5 mμ were obtained by using these apparatuses.

In order to obtain the spectra of moderate intensity, the concentration of the solutions were 20/10000~1.6/10000 mole/l, owing to the path length of the optical vessel. The measurements were performed at the pressures of 1, 1000, 2000 and 3000 kg/cm², and at room temperature, for each solution. The optical densities of each solution at atmospheric pressure were obtained by using the ordinary quartz cell, the path length of which was 1.0 cm.

**Results and Discussion**

*The position and the intensity of the absorption band* The positions and the intensities of absorption maxima of ethyl acetoacetate and acetylacetone in each solvent were investigated at atmospheric pressure, which are due to the enone structure, i.e.

\[-\text{C(OH)}=\text{C} \rightarrow \text{C}-\text{CO}--\]

The results are shown in Figs. 1 and 2, respectively. Figs. 1 and 2 show that the effect of solvent on the keto-enol equilibria of ethyl acetoacetate and acetylacetone at atmospheric pressure, respectively. That is, the keto-enol equilibria of these substances shift to the enol form with decreasing polarity of the solvent.

*Determination of the concentration of the enol form by the spectra* The absorption band of the enol form overlaps with that of the keto form in the region of 240~275 μm. However, the determination of the concentration of the enol form in the given solvent is performed by using the following equation,

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Fig. 1 The ultraviolet spectra of ethyl acetoacetate in the solvent of 1) n-heptane, 2) n-hexane, 3) iso-propanol, 4) ethanol and 5) methanol

Fig. 2 The ultraviolet spectra of acetylacetone in the solvent of 1) n-heptane, 2) n-hexane, 3) iso-propanol, 4) ethanol and 5) methanol

\[
f = f' \frac{E}{100} + f'' \frac{100 - E}{100}, \tag{1}
\]

where \( E \) is the percent concentration of the enol form, \( f \) is the apparent extinction coefficient, \( f' \) and \( f'' \) are the molal extinction coefficients of the enol form and the keto form, respectively. In general, \( f' \) is much larger than \( f'' \) so that \( f'' \) is negligible as compared with \( f' \). Then,

\[
f = f' \frac{E}{100}. \tag{2}
\]

Knowing the values of \( f \) and \( E \), the value of \( f' \) can be calculated by equation (2). On the other hand, for each solution,

\[
\frac{f_p}{f} = \frac{E_p}{E}, \tag{3}
\]

where \( f \) and \( E \) are the apparent extinction coefficient and the concentration of the enol form at atmospheric pressure, respectively, \( f_p \) and \( E_p \) are those of the enol form at the pressure of \( P \). \( f_p \) is corrected for the change of the concentration due to compression. By equation (3), the concentration of the enol form at high pressure can be calculated. For this purpose, the assumption is made. That is, the extinction coefficients do not vary with pressure. Therefore, the change of the apparent extinction coefficient with pressure is due to the change of the keto-enol equilibrium.
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The ultraviolet spectra of ethyl acetooacetate in the solvent of n-hexane at high pressure

Fig. 3  The ultraviolet spectra of ethyl acetooacetate in the solvent of n-hexane at high pressure
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obtained for ethyl acetoacetate in $n$-hexane is shown in Fig. 3 as an example.

In order to determine the concentration of the enol form in each solvent at high pressure, the correction for the change of the concentration due to compression must be done. The concentration at high pressure is shown by the following equation,

$$C^p = m \frac{AS + B_S}{AS} = m \frac{AS}{AS},$$  \hspace{1cm} (4)

where $m$ is the number of moles of solute, $S$ and $S_m$ are the volumes of solvent and solute, respectively, $A$ and $B$ are the relative molal volumes in terms of the volumes at atmospheric pressure, of the solvent and the solute, respectively. $S_m$ is negligible as compared with $S$, for the solutions are very dilute, so that equation (4) is reduced. The relative volumes$^{10}$ of the solvents are shown in Table 2. $f_p$ in each solvent at high pressure is shown in Table 3.

### Table 2 Relative volume at $20^\circ$C ($V_p/V_s$)

<table>
<thead>
<tr>
<th>Pressure (kg/cm$^2$)</th>
<th>methanol</th>
<th>ethanol</th>
<th>iso-propanol</th>
<th>$n$-hexane</th>
<th>$n$-heptane</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>1000</td>
<td>0.931</td>
<td>0.931</td>
<td>0.932</td>
<td>0.909</td>
<td>0.914</td>
</tr>
<tr>
<td>2000</td>
<td>0.888</td>
<td>0.889</td>
<td>0.895</td>
<td>0.864</td>
<td>0.871</td>
</tr>
<tr>
<td>3000</td>
<td>0.859</td>
<td>0.860</td>
<td>0.868</td>
<td>0.834</td>
<td>0.841</td>
</tr>
</tbody>
</table>

### Table 3 $f_p$

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Pressure (kg/cm$^2$)</th>
<th>Ethyl acetoacetate</th>
<th>Acetylacetone</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 1000 2000 3000</td>
<td>1 1000 2000 3000</td>
<td></td>
</tr>
<tr>
<td>methanol</td>
<td>820 740 670 640</td>
<td>8640 7740 7590 8000</td>
<td></td>
</tr>
<tr>
<td>ethanol</td>
<td>1280 1210 1130 1090</td>
<td>9600 9590 9120 9400</td>
<td></td>
</tr>
<tr>
<td>iso-propanol</td>
<td>1560 1520 1580 1640</td>
<td>9500 8950 9950 10270</td>
<td></td>
</tr>
<tr>
<td>$n$-hexane</td>
<td>6960 7000 7080 7190</td>
<td>10300 9850 9800 10350</td>
<td></td>
</tr>
<tr>
<td>$n$-heptane</td>
<td>7080 7160 7200 7290</td>
<td>10700 10390 10820 10820</td>
<td></td>
</tr>
</tbody>
</table>

### Table 4 Keto-enol equilibrium constant

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Pressure (kg/cm$^2$)</th>
<th>Ethyl acetoacetate</th>
<th>Acetylacetone</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 1000 2000 3000</td>
<td>1 1000 2000 3000</td>
<td></td>
</tr>
<tr>
<td>methanol</td>
<td>0.060 0.054 0.048 0.038</td>
<td>2.57 1.82 1.72 1.99</td>
<td></td>
</tr>
<tr>
<td>ethanol</td>
<td>0.096 0.087 0.083 0.081</td>
<td>4.00 3.93 3.17 3.63</td>
<td></td>
</tr>
<tr>
<td>iso-propanol</td>
<td>0.121 0.117 0.122 0.127</td>
<td>3.81 3.90 4.83 5.90</td>
<td></td>
</tr>
<tr>
<td>$n$-hexane</td>
<td>0.923 0.934 0.953 0.984</td>
<td>6.09 4.56 4.46 6.25</td>
<td></td>
</tr>
<tr>
<td>$n$-heptane</td>
<td>0.953 0.976 0.984 0.996</td>
<td>8.17 6.52 8.35 8.35</td>
<td></td>
</tr>
</tbody>
</table>

The concentrations of the enol form in each solvent at high pressure were calculated by equation (3) using the values of \( f_p \). Then, the keto-enol equilibrium constants were also calculated. The results are shown in Table 4 and Figs. 4 and 5 as the keto-enol equilibrium constants.

The keto and enol tautomers of ethyl acetoacetate and acetylacetone are shown in equations (5) and (6), respectively.

\[
\text{H}_3\text{C} \quad \text{C} \quad \text{CH}_2 \quad \text{C} \quad \text{O} \quad \text{C}_2\text{H}_5 \quad \rightleftharpoons \quad \text{H}_3\text{C} \quad \text{C} \quad \text{C} \quad \text{O} \quad \text{C}_2\text{H}_5 \quad (5)
\]

\[
\text{H}_3\text{C} \quad \text{C} \quad \text{CH}_2 \quad \text{CH}_3 \quad \rightleftharpoons \quad \text{H}_3\text{C} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{O} \quad \text{O} \quad H \quad (6)
\]

The parachors\(^{11}\) and the molal volumes of ethyl acetoacetate and acetylacetone were calculated. The parachors were calculated from their atomic structure and then the molal volumes were estimated.

The parachor is represented by equation (7),

$$ P = M r^{1/4} $$

where $M$ is the molecular weight, $D$ and $d$ are the densities of the liquid phase and the gas phase, respectively, and $\gamma$ is the surface tension. In equation (7), $d$ being negligible as compared with $D$ and assuming to be $\gamma = \gamma_0$, then equation (8) is reduced,

$$ P_e D_e = P_k D_k, $$

where suffixes $e$ and $k$ represent the enol form and the keto form, respectively.

Assuming that the density of ethyl acetoacetate in the liquid phase is equal to that of the keto form of ethylacetoacetate, because the keto form is predominant in ethyl acetoacetate, by equation (8), the density of the enol form of ethyl acetoacetate is calculated. Then, the molal volume of the enol form of ethyl acetoacetate is estimated. On the other hand, assuming that the density of acetylacetone in the liquid phase is equal to that of the enol form of acetylacetone, because the enol form is predominant in acetylacetone, by equation (8), the density of the keto form of acetylacetone are calculated. Then, the molal volume of the keto form of acetylacetone is estimated. The results are shown in Table 5. That is, the molal volumes of the enol forms of ethyl acetoacetate and acetylacetone are smaller than those of the keto forms, by $11.0 \sim 13.8$ ml/mole, respectively.

<table>
<thead>
<tr>
<th></th>
<th>Parachor</th>
<th>Molal volume (ml/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl acetoacetate</td>
<td>keto form</td>
<td>303.3</td>
</tr>
<tr>
<td></td>
<td>enol form</td>
<td>277.0</td>
</tr>
<tr>
<td>Acetylacetone</td>
<td>keto form</td>
<td>246.0</td>
</tr>
<tr>
<td></td>
<td>enol form</td>
<td>218.8</td>
</tr>
</tbody>
</table>

The difference of volume between the keto form and the enol form, ($\Delta V = V_k - V_e$) which is estimated by equation (9), is very small in absolute value, and even positive.

$$ \Delta V = -\frac{RT}{P_1 - P_2} \log \frac{K_1}{K_2} $$

In general, the keto-enol equilibria shift to the keto form in the polar solvent, and to the enol form in the non-polar solvent, respectively. According to Powling et al[12], there is a linearity between the free energy change ($\Delta G$) for the keto-enol equilibria of ethyl acetoacetate and acetylacetone, and the dielectric property, $((e-1)/(2e+1))\rho/M$, where $e$, $\rho$ and $M$ are the dielectric constant, the density and molecular weight, respectively.

According to thermodynamics

\[ \ln K = - \frac{\Delta G}{RT}, \]

\[ K = \frac{[\text{Enol}]}{[\text{Keto}]} \]

Then, it is expected that there is a linearity between \( \log K \) and \( \frac{(e-1)/(2e+1)}{p/M} \). Plotting \( \log K \) against \( \frac{(e-1)/(2e+1)}{p/M} \), the results are obtained as shown in Figs. 6 and 7. That is, the keto-enol equilibrium constants decrease with increasing the dielectric constants of the solvents.

![Fig. 6](image1)

![Fig. 7](image2)

Plotting the dielectric constants against pressure\(^{14}\), the results are obtained as shown in Fig. 8. That is, the dielectric constants of the solvents increase with pressure. This view is confirmed by the fact that the absorption spectra show the red shift at high pressure. Assuming that the results as shown in Figs. 6 and 7 hold at high pressure, the keto-enol equilibrium constants decrease with increasing pressure.

\(^{13}\) K. H. Meyer, \textit{Ber.}, \textbf{44}, 2125 (1911), \textbf{45}, 2841 (1912), \textbf{47}, 826 (1914)

\(^{14}\) J. B. Conant and A. F. Thompson, \textit{J. Am. Chem. Soc.}, \textbf{54}, 4039 (1932)


\(^{16}\) S. Kyropoulos, \textit{Z. Physik.}, \textbf{40}, 507 (1927)

\(^{17}\) C. Francke, \textit{Ann. Physik.}, \textbf{77}, 159 (1925)
The effects of pressure on the keto-enol equilibrium constant can be divided into two parts.

I. The volume change of tautomers.

II. The increment of the dielectric constant of the solvent with increasing pressure.

These effects are considered to oppose each other. In the solvents of n-hexane and n-heptane, the increments of the dielectric constants with pressure are small, so that the first effect is preferable. Therefore, the keto-enol equilibria shift to the enol form with pressure. In the solvents of methanol and ethanol, the increments of the dielectric constants with pressure are large, so that the second effect is preferable. Therefore, the keto-enol equilibria shift to keto form with pressure. In the solvent of iso-propanol, the increment of the dielectric constant with pressure is small, so that the keto-enol equilibrium shifts to the enol form at sufficiently high pressure.

The same consideration is adaptable to the effect of pressure on the keto-enol equilibrium of acetylacetone. However, the increment of the equilibrium constant is small. This may be due to the large equilibrium constant even at atmospheric pressure. According to these considerations, the ΔV for ethyl acetoacetate, is 8–10 ml/mole, which seems to be in agreement with the results of parachors.