Introduction

Recently we have carried out $^1$H NMR studies on various carbocyclic π complexes, i.e., ferrocene, azaferrrocene, ruthenocene, etc., to clarify phase transitions, the crystal structure of newly found phases, and the dynamics of the molecule as a whole and the five-membered rings [1–4]. We found that in the crystals the cyclopentadienyl (C₅H₅ : Cp) and pyridinyl (C₅H₄N) rings perform C₅ and pseudo-C₅ reorientations, respectively, with quite different activation energies being mostly determined by intermolecular interactions. This means that, as for the low-temperature stable and substable ferrocene crystals [4], crystal packing is the major origin for the barrier to rotation of the rings.

Acetylferrocene, having an acetyl group attached to one of the Cp rings, is expected to form a rather loosely packed crystal although the bulky acetyl group may create a hindering barrier for the rotation of the Cp rings. Sato et al. [5] studied the crystal structure of this compound at room temperature and below the melting point and proposed that the molecules rotate around the central iron atom at higher temperatures. Early $^1$H NMR investigations, however, had indicated reorientation of the non-substituted Cp rings rather than that of the molecules [5a]. The present investigation has been undertaken to clarify the molecular dynamics of the π complex of solid acetylferrocene.

Experimental

Commercial acetylferrocene was purified three times by sublimation at ca. 60 °C under reduced pressure. X-ray powder patterns by means of an X-ray diffractometer Model D-3F from Rigaku Denki Co. showed that the crystals of the present investigation have exactly the same structure as those employed in the experiments of Sato et al. [5].

The spin-lattice relaxation time $T_1$ of the $^1$H nuclei was determined at various temperatures between 80 and 359 K (m.p.) by use of a homemade pulsed NMR spectrometer [6] operated at the Larmor frequency 20 MHz. A pulse sequence of 180°-τ-90° was employed for the determination of $T_1$. The $T_1$ values observed were estimated to be accurate within ±5% and the temperatures within ±1 K. The differential thermal analysis (DTA) was carried out by use of a homemade apparatus already described [7].

Results and Discussion

According to Sato et al. [5], acetylferrocene forms monoclinic crystals belonging to the space group $P2_1/c$ with $Z = 8$.

From the experiments of differential scanning calorimetry (DSC), Sato et al. [5] found with a very slow heating rate of 0.017 K min⁻¹ two successive phase transitions immediately below the melting point. In our DTA experiments, carried out repeatedly with a heating rate of 0.07 K min⁻¹, however, no heat anom-
A. Kubo et al. • Molecular Dynamics of Solid Acetylferrocene

...aly except that at the m.p. was found. The melting temperature 358 K agreed very well with that reported by Sato et al. [5].

Figure 1 shows the obtained temperature dependence of $^1$H $T_1$ between 80 K and the m.p. at the Larmor frequency of 20 MHz. The $T_1$ curve shows no anomaly just below the m.p., confirming our DTA result, it shows a minimum of 0.07 s at ca. 220 K, a slightly distorted V-shaped curve as compared to the usual BPP one [8], and a maximum of 20 s around 130 K. Below this maximum log $T_1$ decreases almost linearly with $T^{-1}$.

The $^1$H $T_1$ curve indicates that at least two different kinds of motional processes successively occur with increasing temperature and that they partly overlap to form a $T_1$ maximum. The gentle log $T_1$ decrease with increasing $T^{-1}$ is most likely attributable to the CH$_3$ C$_3$ reorientations. This is because the CH$_3$ groups in the acetyl groups always have very small activation energies for the CH$_3$ C$_3$ reorientations [9, 10]. The present assignment is also consistent with the previous $^1$H wide-line NMR results reported by Makova et al. [11].

According to the crystal structure of acetylferrocene, two crystallographically nonequivalent molecules exist in the crystal [5]. This means that there are two kinds of C$_p$ rings having different surroundings in the crystal. In fact, the $T_1$ minimum attributable to the C$_5$ reorientation of the C$_p$ rings is slightly flattened.

We therefore assume two sets of motional parameters for the motion of the C$_p$ rings, namely $i = 1, 2$. The motional parameters of the CH$_3$ C$_3$ reorientation were roughly approximated by only one set ($i = 3$), although there must be two different kinds of CH$_3$ groups in the crystal.

Therefore, to obtain the motional parameters for the CH$_3$ C$_3$ and C$_p$ C$_5$ reorientations, we assume that the observed $^1$H $T_1$ can be expressed as the sum of the three independent BPP curves due to the CH$_3$ C$_3$ and the two kinds of the C$_p$ C$_5$ reorientations given by [12]

$$T_1^{-1} = \frac{3}{2} \gamma \sum_{i=1}^{3} \Delta M_i^2 \left( \frac{\tau_i}{1 + \tau_i^2 \omega_0^2} + 4 \frac{\tau_i}{1 + 4 \tau_i^2 \omega_0^2} \right),$$

(1)

where the correlation times $\tau_i$ for the $i$-th motional mode are assumed to obey the Arrhenius relationships

$$\tau_i = \tau_0^i \exp \left( \frac{E_a^i}{RT} \right).$$

(2)

In (1) and (2), $\gamma$ and $\omega_0$ represent the proton gyromagnetic ratio and the angular Larmor frequency, respectively, and $\Delta M_i^2$, $\tau_0^i$, and $E_a^i$ denote the second moment reduction due to the activation of the $i$-th motional mode of a group, the correlation time of the $i$-th motional mode in the limit of infinite temperature, and its activation energy, respectively.

$\Delta M_3^2$ was calculated to be 5.2 G$^2$ by use of the known crystal data [5]. The intermolecular contribution to $\Delta M_3^2$ was summed up in the same way as employed in [4]. The fitting of (1) and (2) to the observed $T_1$ data was performed by a least-squares method. The calculated curve explains the measurements very well. The motional parameters evaluated are listed in Table 1.

<table>
<thead>
<tr>
<th>Motional Mode ($i$)</th>
<th>$\Delta M_i^2/\gamma G^2$</th>
<th>$E_a^i$/kJ mol$^{-1}$</th>
<th>log$(\tau_0^i)/s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$ reorient. (1)</td>
<td>5.2 (fixed)</td>
<td>4.0 ± 0.2</td>
<td>−13.0 ± 0.2</td>
</tr>
<tr>
<td>C$_p$H$_4$ reorient. (2)</td>
<td>1.5 ± 0.6</td>
<td>21.1 ± 0.6</td>
<td>−13.5 ± 0.2</td>
</tr>
<tr>
<td>(3)</td>
<td>1.6 ± 0.6</td>
<td>23.5 ± 1.3</td>
<td>−13.5 ± 0.2</td>
</tr>
</tbody>
</table>

To check the significance of the motional parameters we calculated $\Delta M_2^2$ for the C$_p$ C$_5$ reorientation using the crystal data [5]. The intermolecular contribution was estimated in a similar way as that used for the evaluation of $M_2$ of the CH$_3$ group. The $M_2$ values calculated for the model in which one kind or two kinds of C$_p$ rings perform C$_5$ reorientation in addition
to the CH$_3$C$_3$ reorientation were found to be 6.3 and 4.8 G$^2$, respectively. This leads to $\Delta M_{2(i)}^0$ equal to 1.5 and 1.6 G$^2$, where $i$ is 1 or 2. So the calculated $\Delta M_{2(i)}^0$ values agree very well with the values obtained from the fitting calculation.

The observed $E_a$ value for the CH$_3$C$_3$ reorientation of acetylferrocene is 4.0 kJ mol$^{-1}$. This is comparable with the data obtained for acetone [10], toluene [13], CH$_3$MC$_13$ ($m$ = Si, Ge, Sn) [14], and dimethylpyridines [15]. However, $E_a$ values for the CH$_3$C$_3$ reorientation of CH$_3$NH$_2^+$ cations in various compounds studied previously [16–20] are much larger than the present value. The $E_a$ values of 21–23 kJ mol$^{-1}$ for the C$_p$C$_5$ reorientation are fairly large for this motion. They are comparable with that of the low-temperature stable orthorhombic phase of ferrocene and are larger than those of triclinic and monoclinic ferrocene.