^{1}H NMR Studies on the Molecular Dynamics of Acetylferrocene in Crystals

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The temperature dependence of ^{1}H spin-lattice relaxation time was determined at 20 MHz for solid acetylferrocene [$(C_5H_5)(C_5H_4COCH_3)Fe$] from ca. 80 K up to the m.p. (359 K). Rather large activation energies of 21 and 24 kJ mol^{-1} for the C_5 reorientations of the two crystallographically nonequivalent non-substituted cyclopentadienyl rings were obtained, indicating that the crystal has a closely packed structure. The two kinds of CH_3 groups attached to the substituted cyclopentadienyl rings were assumed to be approximately equivalent and gave a low activation energy of 4 kJ mol^{-1} for the C_3 reorientation. No phase transition was observed in the relaxation times or in additional experiments of differential thermal analysis although the presence of two phase transitions has been reported previously at temperatures immediately below the melting temperature by means of differential scanning calorimetry.

Introduction

Recently we have carried out ^{1}H NMR studies on various carbocyclic π complexes, i.e., ferrocene, azaferrocene, 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 (C_5H_5: C_p) and pyridinyl (C_4H_4N) rings perform C_5 and pseudo-C_5 reorientations, respectively, with the 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 C_p 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 C_p 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 C_p 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 $180°-\tau-90°$ was employed for the determination of T_1. The T_1 values observed were estimated to be accurate within $\pm 5\%$ 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-

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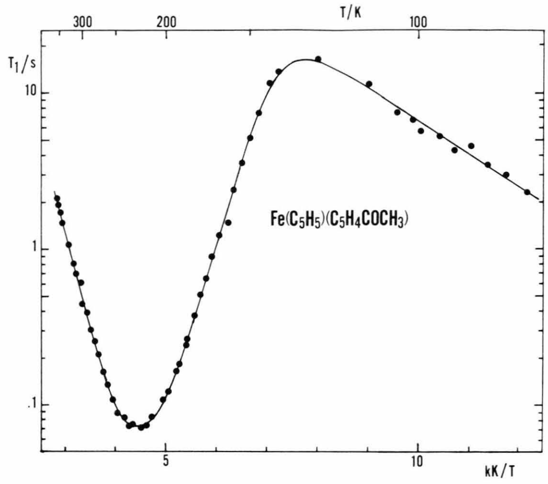

Fig. 1. Temperature dependence of the ^1H spin-lattice relaxation time T_1 observed at 20 MHz for acetylferrocene. Solid line: calculated T_1 curve.

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 ^1H 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 lineary with T^{-1}.

The ^1H 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 ^1H 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.

Table 1. ^1H NMR second moment reduction ΔM_2 for the activation of the three considered modes, their activation energies E_a, and correlation times τ_0.

Motional Mode (i)	$\Delta M_2^{(i)}/G^2$	E_a/kJ mol^{-1}	$\log(\tau_0/s)$
CH_3 reorient. (1)	5.2 (fixed)	4.0 ± 0.2	-13.0 ± 0.2
C_5H_5 reorient. (2)	1.5 ± 0.6	21.1 ± 0.6	-13.5 ± 0.2
(3)	1.6 ± 0.6	23.5 ± 1.3	-13.5 ± 0.2

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 ^1H 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]

$$T_1^{-1} = \frac{3}{2}\gamma \sum_{i=1}^{3} \Delta M_2^{(i)} \left\{ \frac{\tau_i}{1+\tau_i^2\omega_0^2} + \frac{4\tau_i}{1+4\tau_i^2\omega_0^2} \right\}, \qquad (1)$$

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

$$\tau_i = \tau_0^i \exp(E_a^i/RT). \qquad (2)$$

In (1) and (2), γ and ω_0 represent the proton gyromagnetic ratio and the angular Larmor frequency, respectively, and $\Delta M_2^{(i)}$, τ_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.

$\Delta M_2^{(3)}$ was calculated to be 5.2 G^2 by use of the known crystal data [5]. The intermolecular contribution to $\Delta M_2^{(3)}$ 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.

To check the significance of the motional parameters we calculated $\Delta M_2^{(i)}$ 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 $\Delta M_2^{(i)}$ equal to 1.5 and 1.6 G^2, where i is 1 or 2. So the calculated $\Delta M_2^{(i)}$ 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_3MCl_3 (m = Si, Ge, Sn) [14], and dimethylpyridines [15]. However, E_a values for the CH_3 C_3 reorientation of $CH_3NH_3^+$ 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.

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