CHEMISTRY LETTERS, pp. 1497-1500, 1981.

MOTION OF C_5H_5 RINGS IN THREE CRYSTALLINE MODIFICATIONS OF FERROCENE AS STUDIED BY ^1H NMR

Atsushi KUBO, Ryuichi IKEDA, and Daiyu NAKAMURA*
Department of Chemistry, Faculty of Science, Nagoya University,
Chikusa, Nagoya 464

The ^1H spin-lattice relaxation time T_1 at 20 MHz and the second moment of ^1H NMR absorptions were observed at various temperatures for ferrocene in its monoclinic, triclinic, and orthorhombic phases. The barrier to the rotational reorientation of C_5H_5 rings was found to be largest in the orthorhombic phase.

Ferrocene, $Fe(C_5H_5)_2$, is known to undergo a solid state phase transition at 163.9 K,[1)] above and below which temperature it forms monoclinic crystals with the space group $P2_1/a$ ($Z = 2$)[2)] and triclinic ones with $P1$ or $P\bar{1}$ ($Z = 16$),[3-5)] respectively. Recently, Ogasawara et al.[6)] and independently Bérar et al.[7)] carried out a skillful thermal treatment on ferrocene crystals and found a new phase which is stable at low temperatures and is transformed into the monoclinic phase at 242 K. Bérar et al.[7)] also studied the X-ray structural analysis in this new phase of ferrocene and found that the crystal is orthorhombic belonging to the space group $Pnma$ ($Z = 4$).

Commercially available ferrocene was purified by sublimation three times under vacuum. Orthorhombic ferrocene was obtained by the method described in the literature,[6)] and identified by the measurements of DTA. Hereafter, the triclinic, monoclinic, and orthorhombic phases are abbreviated as T, M, and O phases, respectively. Wide-line ^1H NMR spectra were recorded by using a JEOL JNM-MW-40S NMR spectrometer. A home-made pulsed NMR spectrometer[8)] was employed for the determination of the ^1H spin-lattice relaxation time T_1.

The ^1H NMR second moment determined as a function of temperature is shown in Fig. 1 for O and M ferrocene crystals. Below ca. 140 K, O ferrocene yielded an almost constant second moment value

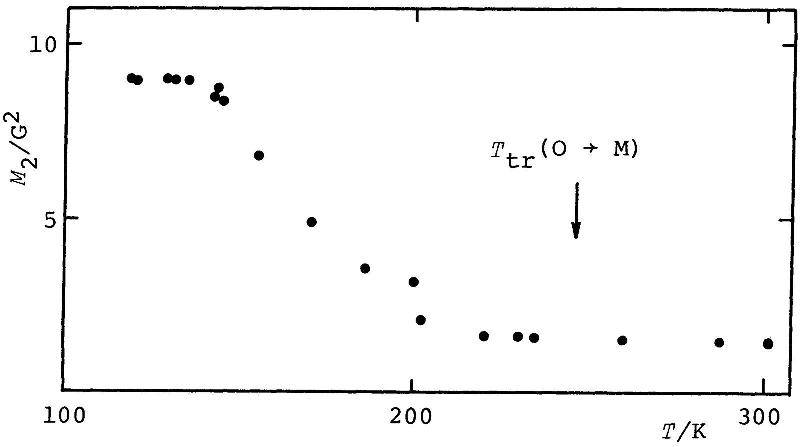

Fig. 1. Temperature dependence of the second moment M_2 of O and M ferrocene crystals.

of ca. 9 G^2. With increasing the temperature from 140 K, the value decreased gradually and reached another constant value of 1.6 G^2 above ca. 210 K. The latter constant value obtained for O ferrocene did not change at the transition temperature $T_{tr}(O \rightarrow M)$ and the same value was obtained for M ferrocene existing above $T_{tr}(O \rightarrow M)$. The present value of 1.6 G^2 observed for M ferrocene agrees very well with the reported experimental values of 1.6 and 1.7 G^2 by Holm and Ibers,[9] and by Mulay and Attalla,[10] respectively.

The temperature variation of T_1 observed for ferrocene crystals is shown in Fig. 2. The T_1 values obtained in M and T phases agree only roughly with those reported by Campbell et al.,[11] because of the poor accuracy of their experimental results. In T phase, a considerably broad T_1 minimum was observed at ca. 110 K. With increasing the temperature from the T_1 minimum temperature, the T_1 value increased monotonously up to $T_{tr}(T \rightarrow M)$. In M phase, however, the T_1 value increased rather gently with increasing temperature. The temperature gradient of the T_1 curve observed in O phase was steeper than that in the other phases, and a T_1 minimum was found for O ferrocene at 238 K.

Since the second moment and also the spin-lattice relaxation rate observed for a protonic system are proportional to r^{-6}, where r stands for the interprotonic distance, pairs of protons having shorter interprotonic distances contribute more to these quantities. In T ferrocene, the shortest interprotonic distance is the intermolecular one having r equal to ca. 2.35 Å,[12] whereas the shortest intra-

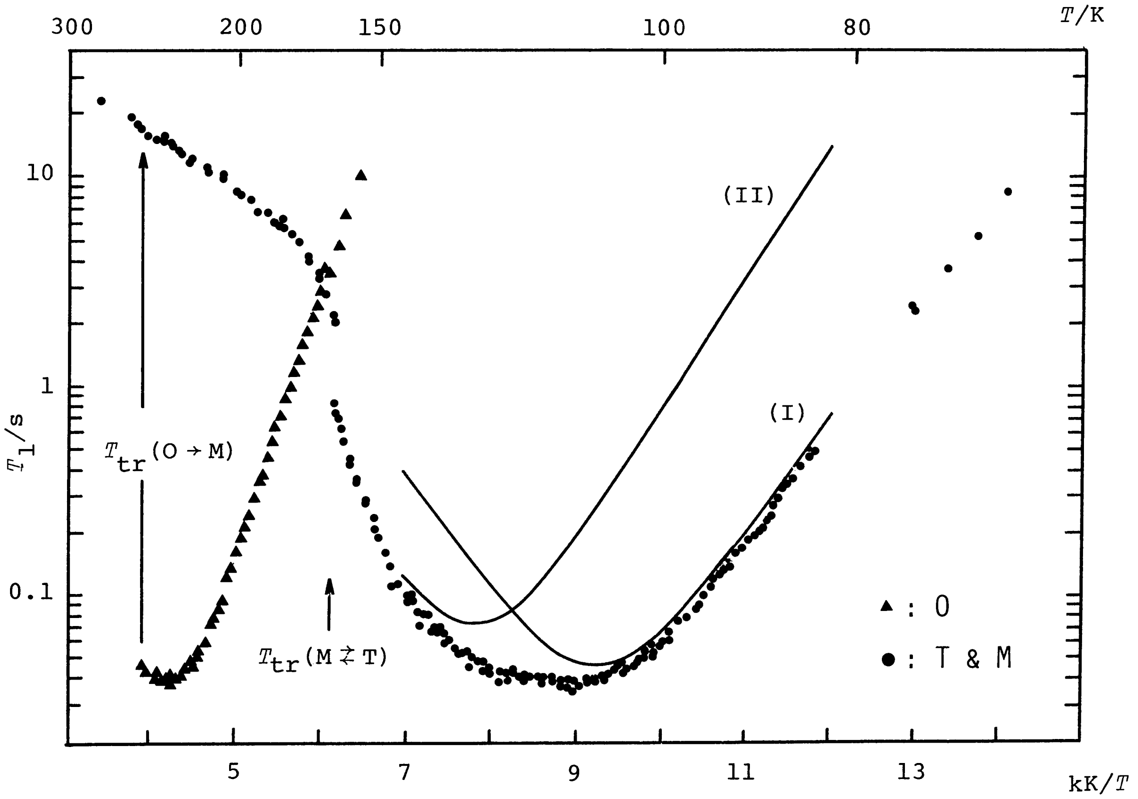

Fig. 2. Temperature dependence of ^1H spin-lattice relaxation time T_1 at 20 MHz in the three modifications of ferrocene.

molecular interprotonic distance is ca. 2.68 Å being found in a C_5H_5 ring of the molecule.[13)] Accordingly, the intermolecular dipolar interaction is more important than the intramolecular one to interprete the second moment or T_1 of ferrocene crystals.

Holm and Ibers[9)] calculated the second moment of polycrystalline ferrocene by a rigid-lattice model constructed based on the reported crystal structure determined at room temperature,[2)] and obtained the values of 5.6 and 2.4 G^2 for the inter- and intramolecular second moments, respectively. The present value of 9 G^2 observed below 140 K in O phase agrees considerably well with the sum of the above calculated values. Orthorhombic ferrocene yielded another constant second moment value of 1.6 G^2 above 200 K. This agrees well with the calculated value of 1.7 G^2 obtained by use of a dynamical model of C_5H_5 rings reorienting about their C_5 axes in M ferrocene.[9)] Therefore, a decrease of the second moment of O ferrocene detected between 140 and 200 K is most probably attributed to the reorientational motion of C_5H_5 rings. A quite similar temperature dependence of the second moment was already reported for T ferrocene.[10)] In this phase, however, the linewidth narrowing takes place at ca. 70 K. Accordingly, it can be concluded that the rotational reorientation of C_5H_5 rings is much more hindered in O ferrocene than in T ferrocene.

The measurements of T_1 in O phase yielded a T_1 curve having a single minimum. This can be analyzed by applying the usual BPP formula. Considering the temperature dependence of the second moment discussed above, the T_1 minimum obtained for O ferrocene can be assigned to the rotational reorientation of the C_5H_5 rings. A rather broad T_1 minimum having almost the same T_1 minimum value as that of O ferrocene was observed for T ferrocene. This indicates that the motional process giving these two T_1 minima seems to be identical i.e., the rotational reorientation of the C_5H_5 rings in the crystal.

The minimum of the T_1 curve of T ferrocene is so broad and also asymmetric that it is impossible to be exactly fitted on a single BPP curve. The T_1 curve, however, can be well interpreted in terms of the sum of two BPP curves (I) and (II) as shown in Fig. 2. This can be explained as that there are two kinds of ferrocene molecules or C_5H_5 groups in the crystal, which are crystallographically different from each other, and they give rise to different proton spin-lattice relaxation. This explanation is fairly probable in view of the results of the X-ray analysis of T ferrocene revealing the existence of two kinds of crystallographically nonequivalent ferrocene molecules in the crystal.[12)]

Table 1. Activation energy E_a for reorientation of C_5H_5 rings about their C_5 axes in ferrocene crystals.

Crystalline phase		E_a/kJmol^{-1}
Orthorhombic (O)		24.8 ± 1.0
Triclinic (T)	(I)	10.3 ± 0.5
	(II)	11 ± 2
Monoclinic (M)		5.4 ± 0.5

The activation energy E_a for the reorientation of the C_5H_5 rings in each ferrocene modification was evaluated by assuming the Arrhenius type relationship as given in Table 1.

The two BPP curves resolved from the T_1 curve observed for T ferrocene yielded almost the same E_a value of ca. 10 kJmol^{-1}. The activation energy determined for M phase was very small (5.4 kJmol^{-1}) as compared with those of the other phases. Since RT (R: the gas constant) amounts to 2.5 kJmol^{-1} at 300 K, it is considered that the C_5H_5 rings in M phase of ferrocene reorient almost freely about their respective C_5 axes at room temperature. Among the three modifications of ferrocene, O ferrocene gives the largest value of E_a for the reorientation of C_5H_5 rings. This is in good agreement with the results of the present second moment experiments and also of the X-ray analysis indicating that the packing of the molecules in O phase is more compact than that in the other phases of ferrocene crystals.7)

Acknowledgment. This work was partially supported by a Grant-in-Aid for Scientific Research No. 543006 from the Ministry of Education, Japan.

References

1) J. W. Edwards, G. L. Kington, and R. Mason, Trans. Faraday Soc., 56, 660 (1960).
2) J. D. Dunitz, L. E. Orgel, and A. Rich, Acta Crystallogr., 9, 373 (1956).
3) J. F. Bérar and G. Calvarin, C. R. Acad. Sci., Ser. C 227, 1005 (1973).
4) G. Calvarin and J. F. Bérar, J. Appl. Cryst., 8, 380 (1975).
5) G. Clec'h, G. Calvarin, J. F. Bérar, and R. Kahn, C. R. Acad. Sci., Ser. C 286, 315 (1978).
6) K. Ogasawara, M. Sorai, and H. Suga, Chem. Phys. Lett., 68, 457 (1979).
7) J. F. Bérar, G. Calvarin, D. Weigel. K. Chhor, and C. Pommier, J. Chem. Phys., 73, 438 (1980).
8) L. S. Prabhumirashi, R. Ikeda, and D. Nakamura, Ber. Bunsenges. Phys. Chem., in press.
9) C. H. Holm and J. A. Ibers, J. Chem. Phys., 30, 885 (1959).
10) L. N. Mulay and A. Attalla, J. Am. Chem. Soc., 85, 702 (1963).
11) A. J. Campbell, C. A. Fyfe, D. Harold-Smith, and K. J. Jeffrey, Mol. Cryst. Liq. Cryst., 36, 1 (1976).
12) P. Seiler and J. D. Dunitz, Acta Crystallogr., B35, 2020 (1979).
13) F. Takusagawa and T. F. Koetzle, Acta Crystallogr., B35, 1074 (1979).

(Received August 21, 1981)