CHEMISTRY LETTERS, pp. 1487-1490, 1982. © The Chemical Society of Japan 1982

STUDIES ON THE NEW CRYSTALLINE PHASE OF AZAFERROCENE AND RUTHENOCENE

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

A new low-temperature phase of azaferrocene $Fe(C_5H_5)(C_4H_4N)$, stable below 281 K, was found from the measurements of proton spin-lattice relaxation time T_1 and differential thermal analysis. For ruthenocene $Ru(C_5H_5)_2$, a phase transition was located at 392 K.

Recently, it was revealed that ferrocene has a low-temperature stable orthorhombic phase below 242 K,[1,2] although its monoclinic phase stable at room temperature is usually supercooled to 163.9 K, below which temperature it forms still metastable triclinic crystals.[3-7] Azaferrocene is known, at room temperature, to form monoclinic crystals isomorphous with those of the room-temperature phase of ferrocene,[8] while ruthenocene to form orthorhombic crystals isomorphous with those of the low-temperature stable phase of ferrocene.[2,9] The existence of crystal modifications such as found in ferrocene would be expected for these sandwich-type compounds. This is the motivation of the present investigation.

The apparatus and methods of the ^1H spin-lattice relaxation time T_1 and differential thermal analysis (DTA) measurements have already been reported.[10,11] The compounds employed were prepared and purified according to the methods described in literature.[8,12] Since azaferrocene was very labile even in a sealed glass ampoule, it was carefully purified by vacuum sublimation at 30°C immediately before use for the measurements. Figure 1 shows the temperature

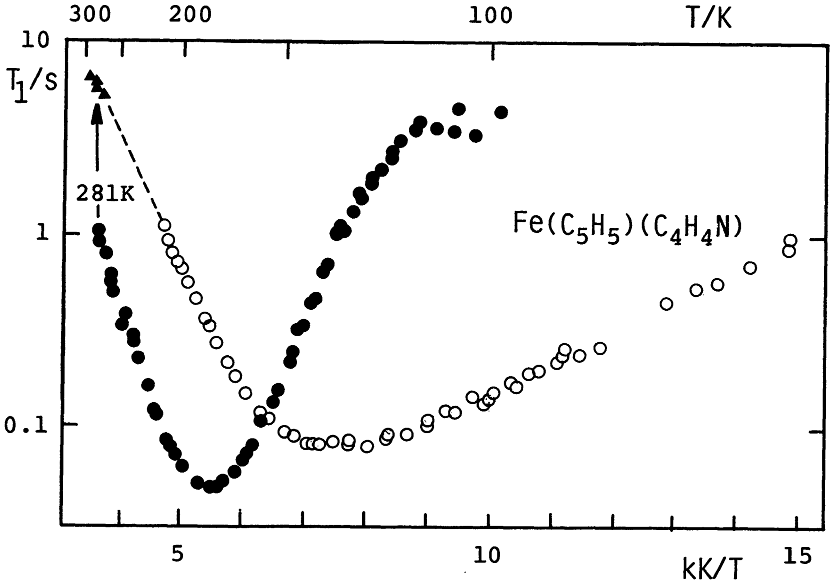

Fig. 1. Temperature dependence of ^1H T_1 at 20 MHz observed for azaferrocene in its three phases: room-temperature stable phase (▲), low-temperature stable phase (●), and low-temperature metastable phase (○).

dependence of ^{1}H T_1 observed for azaferrocene. For the sample treated by cooling it rapidly to 77 K, the T_1 values indicated by open circles were obtained in the temperature range of 65-215 K. When the sample thus obtained was warmed, no single T_1 value could be determined above ca. 215 K. This is because a short T_1 component began to mix with the original long T_1. This coexistence of T_1 values was observed to occur during a time needed for the normal measurement process of T_1 at a fixed temperature. Moreover, the ratio of the long component to the short one decreased continuously with the lapse of time until only the short T_1 value was observed after several tens of minutes at ca. 215 K. The time required for this transformation became shorter with increasing temperature and reached the minimum value of 3 min at ca. 255 K. The completely transformed sample yielded another T_1 curve different from that of the sample prepared by rapid cooling, as indicated by dots in Fig. 1. The appearance of this new curve bears a strong resemblance to that obtained for the orthorhombic phase of ferrocene.13) When the transformed sample was warmed, a longer T_1 component again suddenly appeared at 281 K in addition to the short one. While the sample was kept at this temperature, the longer T_1 component increased its intensity and the short one completely disappeared within ca. 20 min. After that, only the longer T_1 value was observed. This T_1 value increased continuously with increasing temperature.

From these experimental facts, the following conclusions were derived. The room-temperature monoclinic phase of azaferrocene is easily supercooled into a metastable state. The low-temperature stable phase of azaferrocene similar to the orthorhombic phase of ferrocene exists below 281 K, at which temperature it is transformed into the room-temperature stable phase with increasing temperature. The phase transition from the metastable state to the low-temperature stable phase could be observed at any temperature between 215 and 266 K, and required considerable time to complete.

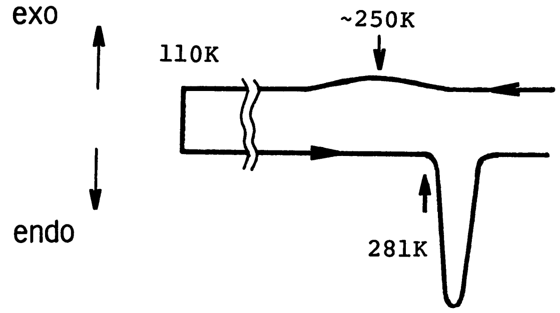

Fig. 2. DTA curves of azaferrocene recorded with a temperature changing rate of ca. 2 K min^{-1}.

These conclusions were confirmed from the results of the DTA experiments. When the temperature was scanned with a rate of ca. 2 K min^{-1}, the DTA curves as shown in Fig. 2 were obtained for azaferrocene. With decreasing temperature, a very broad exothermic anomaly was recorded around 250 K. This anomaly can be well explained by the gradual transition from the supercooled metastable state into the low-temperature stable one revealed from the present NMR study, because almost no anomaly could be observed on the curve recorded with a cooling rate faster than 2 K min^{-1}. With increasing the temperature from 110 K, a big endothermic peak appeared at 281 K in agreement with the transition temperature determined by the proton spin-lattice relaxation measurements.

An anomaly in the T_1 curve of ruthenocene was observed near 390 K as shown in

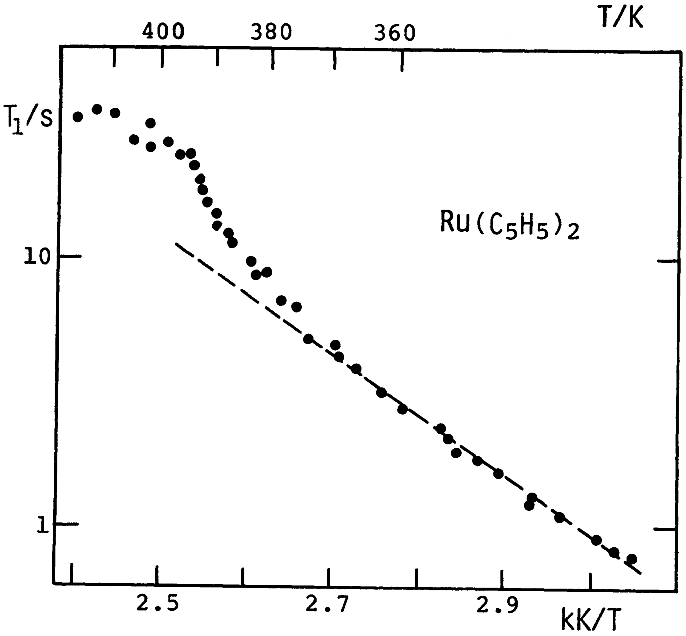

Fig. 3. Temperature dependence of ^{1}H T_1 at 20 MHz observed for ruthenocene.

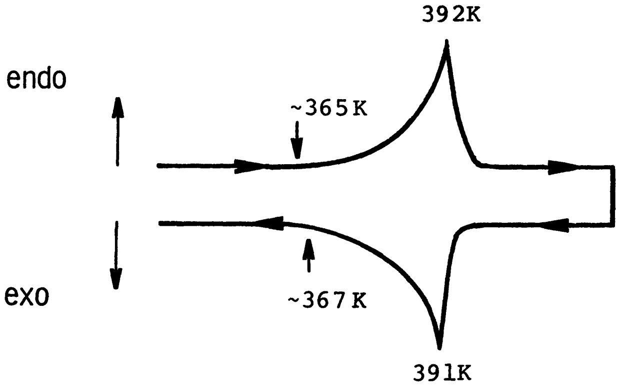

Fig. 4. DTA curves obtained for ruthenocene.

Fig. 3. With increasing temperature, the T_1 value increased unusually above ca. 370 K. On warming further, although the T_1 value itself changed continuously, the temperature gradient of the T_1 curve changed markedly at ca. 394 K, suggesting the existence of a phase transition. With decreasing temperature, the reverse process of the temperature dependence of T_1 could be exactly followed, suggesting that the phase transition is a second-order one.

To confirm the presence of the phase transition in ruthenocene crystals, the measurements of DTA were carried out. The results are shown in Fig. 4. The heat anomalies, which appear at approximately the same temperature in both of the cooling and heating runs, have a long tail on the low-temperature side. DTA curves showing this feature have already been observed for some methylammonium salts.[11,14-16] For these compounds, transition temperatures associated with such DTA anomalies were determined by reading the peak position of the DTA curve recorded on the heating run. This is because the temperature dependence of the nuclear quadrupole resonance frequencies of halogens observed for some of these methylammonium salts yielded a clearly determinable anomaly at the identical temperature as that of the peak position of such DTA curves.[11,14-17] Therefore, it is concluded that ruthenocene undergoes a second-order or higher-order phase transition at 392 K.

Acknowledgment. This work was partially supported by a Grant-in-Aid for Scientific Research No. 00543006 from the Japanese Ministry of Education, Science and Culture.

References

1) K. Ogasahara, M. Sorai, and H. Suga, Chem. Phys. Lett., 68, 457 (1979); Mol. Cryst. Liq. Cryst., 71, 189 (1981).
2) J. F. Bérar, G. Calvarin, D. Weigel, K. Chhor, and C. Pommier, J. Chem. Phys., 73, 438 (1980).
3) J. W. Edwards, G. L. Kington, and R. Mason, Trans. Faraday Soc., 56, 660 (1960).
4) J. D. Dunitz, L. E. Orgel, and A. Rich, Acta Crystallogr., 9, 373 (1956).
5) J. F. Bérar and G. Calvarin, C. R. Acad. Sci., Ser. C 277, 1005 (1973).
6) G. Calvarin and J. F. Bérar, J. Appl. Crystallogr., 8, 380 (1975).
7) G. Clec'h, G. Calvarin, J. F. Bérar, and R. Kahn, C. R. Acad. Sci., Ser. C 286, 315 (1978).
8) K. K. Joshi, P. L. Pauson, A. R. Qazi, and W. H. Stubbs, J. Organomet. Chem., 1, 471 (1964).
9) G. L. Hardgrove and D. H. Templeton, Acta Crystallogr., 12, 28 (1959).
10) L. S. Prabhumirashi, R. Ikeda, and D. Nakamura, Ber. Bunsenges. Phys. Chem., 85, 1142 (1981).
11) Y. Kume, R. Ikeda, and D. Nakamura, J. Magn. Reson., 33, 331 (1979).
12) D. E. Bublitz, W. E. McEwen, and J. Kleinberg, Org. Synth., 41, 96 (1961).
13) A. Kubo, R. Ikeda, and D. Nakamura, Chem. Lett., 1981, 1497.
14) Y. Kume, R. Ikeda, and D. Nakamura, J. Phys. Chem., 82, 1926 (1978).
15) H. Ishida, R. Ikeda, and D. Nakamura, Phys. Stat. Sol., (a) 60, K115 (1980); J. Phys. Chem., 86, 1003 (1982).
16) H. Ishida, R. Ikeda, and D. Nakamura, Phys. Stat. Sol., (a) 70, K151 (1982).
17) G. Jugie and J. A. S. Smith, J. Chem. Soc., Faraday Trans., 2, 74, 994 (1978).

(Received July 14, 1982)