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THE STUDY OF MOLECULAR MOTIONS IN SUBSTITUTED FERROCENES BY MEANS OF NMR SPECTROSCOPY

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SUMMARY

The proton magnetic resonance spectra for ferrocene derivatives have been investigated in the solid state at a frequency of 27.5 MHz and at temperatures within the range 4.2–300 K. Evidence for re-orientation in various substituent groups and cyclopentadienyl rings has been deduced on the basis of the temperature dependence of the second moment of the PMR lines. The experimentally observed decrease in the second moment has been compared with the calculated contributions of different molecular groups to the second moment thus enabling an identification of these groups. In computing the second moment, account has been taken of both intra- and intermolecular dipole–dipole interactions. It is shown that the introduction of substituents into some ferrocene rings affects the magnitude of the re-orientation energy for both the substituted and unsubstituted rings. The change of the re-orientation energy of the substituted and unsubstituted rings in substituted ferrocenes with the structure and electronic properties of the substituents is discussed.

INTRODUCTION

The study of re-orientation processes in the cyclopentadienyl (Cp) rings of ferrocene[1,2], nickelocene, cobaltocene and its cation[3] has shown that the rate of re-orientation becomes comparable with the PMR line-width at 55–65 K. A sharp decrease in the second moment of the PMR line for these compounds over a narrow temperature range enables the determination of the activation energy of the re-orientation process. This has been found to be 2.0±0.2 kcal·mole^{-1} for $Fe(C_5H_5)_2$[1,2] and 1.8±0.2 kcal·mole^{-1} for $Ni(C_5H_5)_2$[3] and $Co(C_5H_5)_2$[3]. Arising from these studies, it would be interesting to investigate the effect of various substituents upon the mobility of both substituted and unsubstituted Cp rings in ferrocene and to compare the rates of the re-orientation processes and electronic structures of the ferrocene derivatives.

RESULTS

The proton resonance spectra have been measured over the temperature range 4.2–300 K at 27.5 MHz. The appearance of re-orientation in various substituent

TABLE 1

ACTIVATION ENERGIES FOR THE RE-ORIENTATION OF METHYL AND Cp PROTONS IN FERROCENE DERIVATIVES TOGETHER WITH THE CORRESPONDING CORRELATION TIMES

Compounds	*Methyl protons*		*Cp protons (unsubst. ring)*		*Cp protons (subst. ring)*		M^2 (*calcd.*) (Oe^2)	M^2 (*exper.*) (Oe^2)
	τ_0 (*sec*)	E_{act} (*kcal·mole*$^{-1}$)	τ_0 (*sec*)	E_{act} (*kcal·mole*$^{-1}$)	τ_0 (*sec*)	E_{act} (*kcal·mole*$^{-1}$)		
$(C_5H_5)_2Fe$			1.2×10^{-13}	2.0				
$C_2H_5C_5H_4FeC_5H_5$	4.9×10^{-14}	1.8	1.2×10^{-13}	3.4		8.2	14.7	14.7 ± 2.0
$i\text{-}C_3H_7C_5H_4FeC_5H_5$	5.7×10^{-14}	3.9	1.3×10^{-13}	7.9		9.5	19.9	25.0 ± 4.0
$t\text{-}C_4H_9C_5H_4FeC_5H_5$	7.1×10^{-14}	4.6	8.2×10^{-14}	8.4		9.5	21.0	28.0 ± 4.0
$(t\text{-}C_4H_9C_5H_4)_2Fe$	5.3×10^{-14}	3.5			1.1×10^{-14}	6.8	24.0	31.0 ± 5.0
$CH_3COC_5H_4FeC_5H_5$	1.17×10^{-13}	2.9	1.1×10^{-13}	5.5		>11.0	12.1	11.7 ± 2.0
$(CH_3COC_5H_4)_2Fe$	1.9×10^{-14}	1.5				>11.0	14.7	13.8 ± 2.0

groups and Cp rings has been deduced from the temperature dependence of the second moment of the PMR line. The observed decrease of the second moment in the above or other temperature regions has been compared with the calculated contributions of different molecular groups towards the second moment, thus enabling an identification of these groups. In calculating the second moments, account has been taken of both inter- and intramolecular dipole–dipole interactions. The intramolecular interaction was computed by a well established procedure[4] using the known molecular configurations of the various compounds. For ferrocene the measured intermolecular contribution was found to be 5.6 Oe^{3}[1] leading to a contribution of 3 Oe^{2} for the CH_3 group[5]. On the basis of these values, an intermolecular contribution to the second moment has been determined for each compound with the inclusion of a weighting factor for the protons of the Cp rings and the methyl groups. The computed second moments for a rigid lattice and the values observed at 4.2 K are given in Table 1. The second moment of the PMR lines was determined with an accuracy of 15–20%. Activation energies for the re-orientation processes involving the methyl and Cp protons as estimated from the experimental data are also shown in Table 1.

The following conclusions may be reached:

(*a*) The computed second moment for the rigid lattice of ethylferrocene is in good agreement with the observed value. The re-orientation of the ethyl protons at 50–60 K is mainly responsible for the decrease of the second moment component (which results from the methyl and methylene protons) to three quarters of its value for the rigid lattice[6]. The appearance of re-orientation in one ferrocene ring leads to a two-fold decrease in the second moment of the Cp protons[2]. Apparently this provides an explanation for the lower second moment of ethylferrocene at 75–85 K (Table 2) (from 9.7 Oe^{2} to 7.1 Oe^{2}). A further decrease in the second moment due to a re-orientation of the substituted ring and an increase in the amplitude of the molecular vibrations occurs above 210 K and up to 258 K where ethylferrocene liquefies.

(*b*) In ferrocenes with tert-butyl substituents, the computed second moment is considerably less than the experimental value (Table 1). One of the reasons for such a deviation could be that, in practice, a contribution to the second moment from an intermolecular interaction is somewhat greater than the computed value. In the

TABLE 2

TEMPERATURE RANGES (K) OVER WHICH CHANGES IN THE SECOND MOMENT OCCUR

Compounds	*Methyl protons*	*Cp protons*	
		Unsubst. ring	*Subst. ring*
$(C_5H_5)_2Fe$		65–75	
$C_2H_5C_5H_4FeC_5H_5$	45–55	75–85	210
$i\text{-}C_3H_7C_5H_4FeC_5H_5$	70–140	205–215	245
$t\text{-}C_4H_9C_5H_4FeC_5H_5$	70–150	200–220	245
$(t\text{-}C_4H_9C_5H_4)_2Fe$	70–125		170–180
$CH_3COC_5H_4FeC_5H_5$	90–150	190–220	300
$(CH_3COC_5H_4)_2Fe$	40–50		300

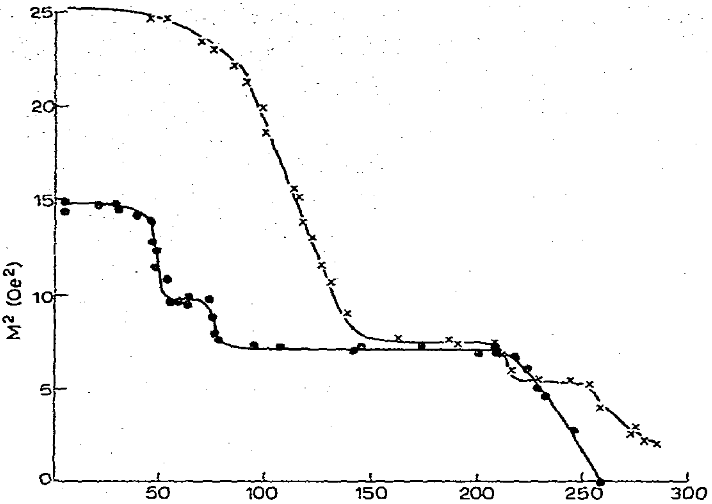

Fig. 1. Temperature dependence of the second moment of the PMR lines for ethylferrocene (●) and isopropylferrocene (×).

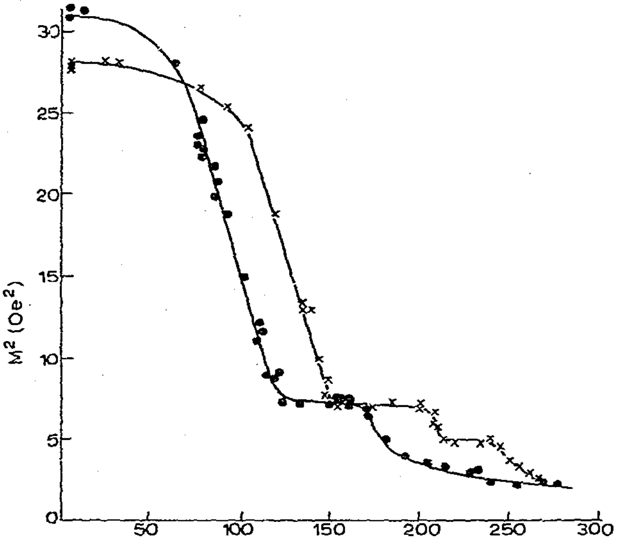

Fig. 2. Temperature dependence of the second moment of the PMR lines for tert-butylferrocene (×) and 1,1′-di-tert-butylferrocene (●).

region 70–140 K, a decrease in the second moment for isopropyl-, tert-butyl- and 1,1′-di-tert-butylferrocenes may be attributed to re-orientation of the methyl protons (Figs. 1 and 2). The value of second moment, 7.5 Oe^2, remains constant for isopropyl- and tert-butylferrocene up to 210–215 K, but above this temperature the second moment again decreases by approximately 2 Oe^2 which corresponds to a re-orientation of the unsubstituted Cp ring. Movement of the substituted Cp ring occurs in both compounds above 240 K. For 1,1'-di-tert-butylferrocene, re-orientation of both Cp rings occurs at a somewhat lower temperature (Fig. 2). The further decrease of the second moment at 170 K is probably due to other molecular motions besides those generated by Cp ring re-orientation.

(*c*) Of the ferrocene compounds investigated, acetyl- and 1,1'-diacetylferrocene are those which contain electron-attracting substituents. The influence of temperature on the change of the second moment is probably related to differences in the re-orientation processes involving the Cp rings of these compounds relative to the ferrocenes discussed above. Re-orientation of methyl protons in acetylferrocene over the temperature range 90–150 K leads to a decrease in the second moment of over 4 Oe^2 (Fig. 3). The decrease of the second moment of 3 Oe^2 which occurs at 190 K is probably due to re-orientation in the unsubstituted ring. The substituted ring in acetylferrocene remains unchanged up to 300 K. The decrease in the second moment by 2.5 Oe^2 in 1,1'-diacetylferrocene at 40–50 K is obviously due to re-orientation of the methyl protons, the substituted ring remaining virtually unchanged up to 300 K.

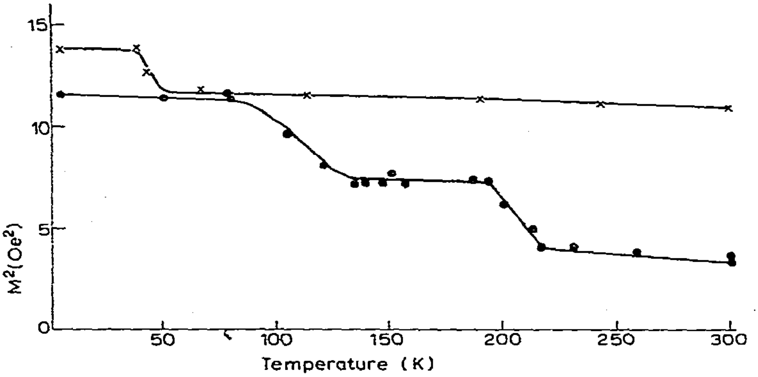

Fig. 3. Temperature dependence of the second moment of the PMR lines for acetylferrocene (●) and 1,1'-diacetylferrocene (×).

DISCUSSION

From the data presented, it follows that introduction of a substituent into one of the rings of ferrocene has a marked effect on the re-orientation of the unsubstituted ring. The movement of this ring becomes much more hindered, the activation energy increasing to 8 kcal·mole^{-1} relative to the value of 2 kcal·mole^{-1} for the initial ferrocene molecule. Apparently introduction of a substituent distorts the symmetry of the electron density distribution among the Cp rings of the asymmetrically substituted ferrocene. Such a distortion may be responsible for the greater activation energy observed for the protons in the unsubstituted ring in monosubstituted ferrocene. This distortion is partially removed by the introduction of a second substituent into the ferrocene molecule. In fact in 1,1'-di-tert-butylferrocene the presence of two bulky groups causes no increase in the re-orientation temperature of the Cp protons but conversely this temperature is much less than the corresponding value for that of tert-butylferrocene.

The introduction of a succession of bulky substituents (C_2H_5, i-C_3H_7, t-C_4H_9) into one of the ferrocene rings gradually decreases the activation energy required for proton re-orientation in the substituted Cp ring and the temperature at which the rate of ring re-orientation becomes comparable with the PMR line-width of these compounds. On the other hand the introduction of the acetyl group which is sterically similar to the isopropyl group considerably enhances the activation energy for the substituted Cp ring protons.

Among the reasons for this phenomenon, the possibility of a mesomeric structure for acetylferrocene in which the acetyl group interacts with the Cp ring should be mentioned. The appearance of new intense band in the UV spectrum of acetylferrocene at 310 nm which exhibits a "red shift" in passing from a non-polar to a polar solvent may also be advanced in support of this suggestion[7].

Introduction of the second acetyl group into acetylferrocene causes virtually no change in the value of the second moment at 4.2–300 K. It is known that in crystalline 1,1′-diacetylferrocene the acetyl groups are located in the 1,3′ positions[8]. In addition, no intra- or intermolecular hydrogen bonding was observed in this molecule. All these data indicate that steric factors alone cannot explain the considerable increase observed in the activation energy for the re-orientation of the ring protons in 1,1′-diacetylferrocene. It is quite obvious that an intramolecular charge transfer must be invoked to explain the behaviour of diacetylferrocene.

It should be pointed out that analysis of X-ray data for different ferrocenes[9] including 1,1′,3,3′-tetra-tert-butylferrocene[10] has shown that within the accuracy of the experiment there is no correlation between the size and character of substituent and the Fe–C distance. The latter value remained constant to within experimental accuracy. In addition, the packing density of 1,1′,3,3′-tetra-tert-butylferrocene and 1,1′-diacetylferrocene crystals is not essentially different from that of ferrocene[10]. In spite of the fact that the above study of re-orientation processes in ferrocene derivatives was carried out in the solid state, the conclusions obtained show that intermolecular interactions in the compounds investigated are approximately equal. For this reason it must be assumed that differences in the behaviour of these compounds must arise from differences in intramolecular interaction and/or in their electronic structures.

REFERENCES

1 C. H. Holm and I. A. Hers, *J. Chem. Phys.*, 30 (1959) 885.
2 L. N. Mulay and A. Attala, *J. Amer. Chem. Soc.*, 85 (1963) 702.
3 M. K. Makova, Yu. S. Karimov, N. S. Kochetkova and E. V. Leonova, *Teor. Eksp. Khim.*, 8 (1972) 259.
4 J. H. Von Vleck, *Phys. Rev.*, 74 (1948) 1168.
5 H. S. Hutowsky and G. E. Pake, *J. Chem. Phys.*, 18 (1950) 162.
6 J. L. Carolon and T. A. Scott, *J. Magn. Resonance*, 2 (1970) 243.
7 G. B. Zaslavskaya, B. M. Yavorskii, N. S. Kochetkova and N. P. Gambaryan, *Dokl. Akad. Nauk SSSR*, 179 (1968) 589.
8 G. J. Palenik, *Inorg. Chem.*, 9 (1970) 2424.
9 M. R. Churchill and J. Wormold, *Inorg. Chem.*, 8 (1969) 719.
10 Z. L. Kaluski, Ju. T. Struchkov and A. J. Gusev, *Bull. Acad. Pol. Sci.*, 21 (1973)