A Determination of the Activation Energy of Cyclopentadienyl Group Rotation and Molecular Tumbling in $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4R)]$ (R = CMe_2Et or Bu^n) using Carbon-13 Nuclear Magnetic Resonance Relaxation Measurements †

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From variable-temperature ^{13}C spin-lattice relaxation time and nuclear Overhauser enhancement measurements in $[^2H_8]$toluene solution at 25 and 100 MHz, the activation energies for ring rotation and molecular tumbling have been determined for n-butylferrocene and t-pentylferrocene.

Although solution nuclear magnetic relaxation measurements have been applied extensively to organic molecules to investigate molecular tumbling and internal rotation,[1] there have only been a few such studies of organometallic compounds.[2] These studies have been dominated by the investigation of methyl group rotation, although there has also been a study made of phenyl rotation in SiH_3Ph.[3] Only one investigation of the rotation of a π-complexed ligand has been reported, namely the cyclopentadienyl group in $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Bu^n)]$ and $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4COMe)]$, but only the relative rates of motion of the two rings were determined.[4]

In most of these studies spin-lattice relaxation times, T_1, were used to determine the speed of motion of each part of the molecule and hence the activation energies for motion. Of the several methods used, the use of the dipole–dipole component of the carbon-13 T_1 requires the least number of assumptions, namely an estimate of the carbon–hydrogen bond length, and that molecular tumbling is isotropic. Consequently this approach is adopted in this work.

Ferrocene derivatives were chosen for examination as there are several solid-state and gas-phase studies available which give the activation energy for cyclopentadienyl rotation.[5–7] For ferrocene in the solid state, E_a for ring rotation has been determined as 2.0 ± 0.3 kcal mol^{-1}.

Experimental

The n-butylferrocene and t-pentylferrocene were purchased from I.C.N. Pharmaceuticals, Inc., and Aldrich Chemical Co., Inc., respectively. Both compounds were vacuum distilled, prior to redistilling into 10-mm n.m.r. tubes, equipped with vortex plugs. $[^2H_8]$Toluene was then distilled in to give a *ca.* 20% solution, and the tubes sealed under vacuum, to give sample volumes of *ca.* 1.3 cm^3 below the vortex plug.

Carbon-13 relaxation and nuclear Overhauser enhancement (n.O.e.) measurements were carried out on a JEOL PFT-100 at 25.15 MHz and on a Bruker WH-400 n.m.r. spectrometer at 100.62 MHz. The relaxation measurements were performed using the π–τ–$\pi/2$ pulse sequence, waiting at least $8T_1$ between each cycle. Effects of machine instability were minimised in the case of the JEOL spectrometer by placing the chosen values of the pulse interval (τ) in an arbitrary order, with short and long rather than the more usual increasing order. For the Bruker instrument, disc-based averaging was used so that eight spectra with the first τ value were acquired, stored on disc, then a second block of eight spectra with the second τ value were acquired and stored on disc. This procedure was repeated until data for all the τ values had been measured. Then the whole procedure was repeated, adding to the data previously stored on disc until a satisfactory signal to noise ratio had been achieved. These measurements were only performed for the three different proton-bearing cyclopentadienyl carbon atoms.

For the nuclear Overhauser measurements, the standard gated decoupling procedure was used. In the case of the JEOL, no procedure was available to reduce errors due to machine instability, and errors in n.O.e. measurements were frequently large. For the Bruker WH-400, errors were minimised by disc-based averaging.

Temperature measurements were performed using a thermocouple in a 10-mm n.m.r. tube containing toluene and a thermocouple attached to a Comark 1625 analogue or 5235 digital thermometers. In the case of the JEOL PFT-100, temperature equilibration took 15 min but for the Bruker WH-400, over 1 h was required. The major time delay arose from waiting for the electrical components in the 43—170 MHz probe to come to constant temperature so that the tuning of the probe became constant.

Results and Discussion

As a result of the substituent on one of the cyclopentadienyl rings in $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4R)]$ (R = Bu^n or CMe_2Et), one ring moves relatively slowly due to the 'anchoring' effect of the substituent into the solvent, see Table 1. Thus T_1 of the unsubstituted cyclopentadienyl group, which is moving faster than the substituted ring due to rotation, is significantly longer than for the substituted ring. In each case the dipole–dipole component of T_1, T_{1dd}, can be calculated from T_1 (observed) and the nuclear Overhauser enhancement. The standard equation, assuming $\omega^2\tau_c^2 \ll 1$, can be written as equation (1) where μ_0^2 is the permittivity of a vacuum, γ_H is

$$T_{1dd}^{-1} = \frac{\mu_0^2\gamma_H^2\gamma_C^2 h^2 S(S+1)\tau_c}{12\pi^2 r_{CH}^6} \qquad (1)$$

the gyromagnetic ratio of the proton, γ_C is the gyromagnetic ratio of the ^{13}C nucleus, *h* is Planck's constant, *S* is the proton spin quantum number, τ_c is the correlation time, and r_{CH} is the carbon–hydrogen bond length.[8] Apart from τ_c, all these terms are known, permitting the direct calculation of τ_c from the experimentally determined T_{1dd} value, see Table 2. Even the longest value of τ_c, 60.8×10^{-12} s, has $\omega^2\tau_c^2 = 0.006$, *i.e.* $\ll 1$. From the temperature dependence of τ_c of the substituted

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† *Non-S.I. unit employed:* cal. = 4.184 J.

Table 1. Carbon-13 relaxation data for n-butylferrocene and t-pentylferrocene in [$^2H_8$]toluene

Temperature (°C)	Cyclopentadienyl group	T_1/s	$1 + \eta$ [a]
(*a*) n-Butylferrocene at 100.62 MHz			
65.5	C_5H_5	15.0	2.89
	$C_5H_4Bu^n$	9.4 [b]	2.92
		10.1 [c]	3.03
50	C_5H_5	13.15	2.73
	$C_5H_4Bu^n$	7.88 [b]	2.73
		8.49 [c]	2.73
22	C_5H_5	9.21	2.78
	$C_5H_4Bu^n$	5.22 [b]	2.83
		5.56 [c]	2.89
2	C_5H_5	6.75	2.74
	$C_5H_4Bu^n$	3.68 [b]	2.80
		3.98 [c]	2.86
−22	C_5H_5	3.93	2.73
	$C_5H_4Bu^n$	1.94 [b]	2.78
		2.38 [c]	2.83
−43.5	C_5H_5	2.70	2.60
	$C_5H_4Bu^n$	1.45 [b]	3.00
		1.33 [c]	2.53
−58.5	C_5H_5	1.51	2.61
	$C_5H_4Bu^n$	0.80 [b]	2.84
		0.83 [c]	2.80
(*b*) t-Pentylferrocene at 25.15 MHz			
56	C_5H_5	20.0	
	$C_5H_4CMe_2Et$	12.50 [d]	
		14.30 [e]	
24	C_5H_5	10.47	
	$C_5H_4CMe_2Et$	6.27 [d]	
		6.77 [e]	
−4	C_5H_5	6.63	
	$C_5H_4CMe_2Et$	3.91 [d]	
		4.20 [e]	
−45.5	C_5H_5	2.53	
	$C_5H_4CMe_2Et$	1.21 [d]	
		1.22 [e]	

[a] The term η is the nuclear Overhauser enhancement. [b] At δ 68.4. [c] At δ 67.4. [d] At δ 67.0. [e] At δ 65.8.

ring the application of the Arrhenius and Eyring equations leads to $E_a = 2.82 \pm 0.07$ kcal mol^{-1}, log $A = 13.11 \pm 0.26$, $\Delta H^\ddagger = 2.28 \pm 0.09$ kcal mol^{-1}, $\Delta S^\ddagger = -0.32 \pm 0.32$ cal K^{-1} mol^{-1}, and $\Delta G_{300}^\ddagger = 2.38$ kcal mol^{-1} for molecular tumbling. A similar analysis for [Fe(η^5-C_5H_5)(η^5-$C_5H_4CMe_2Et$)] yields $E_a = 3.63 \pm 0.10$ kcal mol^{-1}, log $A = 13.64 \pm 0.58$, $\Delta H^\ddagger = 2.89 \pm 0.15$ kcal mol^{-1}, $\Delta S^\ddagger = 2.10 \pm 0.58$ cal K^{-1} mol^{-1}, and $\Delta G_{300}^\ddagger = 2.26$ kcal mol^{-1}.

In order to analyse the internal rotation of the unsubstituted cyclopentadienyl ring, isotropic molecular tumbling was assumed as the molecule is approximately spherical. For methyl group rotation in a variety of organic molecules, equations (2) and (3) have been derived [9] where θ is the angle

$$T_{1dd}^{-1} = \frac{\mu_0^2 h^2 \gamma_H^2 \gamma_C^2 S(S+1)\chi\tau_c}{12\pi^2 r_{CH}^6} \qquad (2)$$

$$\chi = \tfrac{1}{4}(3\cos^2\theta - 1)^2 + 18(5+\rho)^{-1}\sin^2\theta\cos^2\theta + \tfrac{9}{4}(1+2\rho)^{-1}\sin^4\theta \qquad (3)$$

between the rotation axis and the C–H bond and τ_m is the correlation time for the intramolecular rotation. For a cyclopentadienyl group, θ is taken as 85.4° on the basis of a

Table 2. Calculated correlation times, τ_c, and cyclopentadienyl ring rotation times, τ_m, for n-butylferrocene and t-pentylferrocene

Temperature (°C)	$10^{12}\tau_c$/s	$10^{12}\tau_m$/s
(*a*) n-Butylferrocene		
65.5	5.5	3.5
50	5.7	3.7
22	9.3	4.1
2	12.9	5.4
−22	22.8	8.5
−43.5	34.2	9.5
−58.5	60.8	16.9
(*b*) t-Pentylferrocene		
56	4.0	3.4
24	8.2	5.4
−4	13.2	8.1
−45.5	44.2	13.1

microwave structure determination on ferrocene; ρ is given by equation (4). As $\chi = T_{1dd}(C_5H_4R)/T_{1dd}(C_5H_5)$, ρ, and hence

$$\rho = (\tau_c + \tau_m)/\tau_c \qquad (4)$$

τ_m can be readily calculated, see Table 2. The temperature dependence of τ_m gives the activation energy for cyclopentadienyl rotation. For [Fe(η^5-C_5H_5)(η^5-$C_5H_4Bu^n$)], this analysis gives $E_a = 1.91 \pm 0.14$ kcal mol^{-1}, log $A = 12.74 \pm 0.56$, $\Delta H^\ddagger = 1.24 \pm 0.17$ kcal mol^{-1}, $\Delta S = -1.47 \pm 0.64$ cal K^{-1} mol^{-1}, and $\Delta G_{300}^\ddagger = 1.98$ kcal mol^{-1} for cyclopentadienyl rotation

[Fe(η^5-C_5H_5)(η^5-$C_5H_4CMe_2Et$)] was investigated using a JEOL PFT-100 spectrometer where the measurement of the nuclear Overhauser effect is subject to a 10% error. As a consequence and as the magnitude showed the dipole–dipole mechanism to be dominant, it was assumed that the relaxation is exclusively dipole–dipole. This treatment then led to an almost identical set of activation energies for cyclopentadienyl ring rotation: $E_a = 2.44 \pm 0.22$ kcal mol^{-1}, log $A = 13.09 \pm 0.91$, $\Delta H^\ddagger = 1.39 \pm 0.23$ kcal mol^{-1}, $\Delta S^\ddagger = -2.19 \pm 0.84$ cal K^{-1} mol^{-1}, and $\Delta G_{300}^\ddagger = 2.05$ kcal mol^{-1}.

The values for activation energies for cyclopentadienyl ring rotation obtained from solution ^{13}C relaxation measurements are in good agreement with solid-state measurements.[5–7]

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