Journal of Organometallic Chemistry, 405 (1991) 347–355
Elsevier Sequoia S.A., Lausanne
JOM 21417

Carbon-13 spin-lattice relaxation in iron sandwich complexes and related species

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(Received August 24th, 1990)

Abstract

Spin-lattice relaxation times (T_1) are reported for a series of ferrocene derivatives and related sandwich complexes. These values have been used to investigate the relative importance of overall molecular reorientation (tumbling, correlation time τ_c) and internal rotational motions (τ_m). A series of sterically crowded ferrocenes were examined and τ_m/τ_c ratios obtained. For triphenylmethylferrocene derivatives all internal rotations appear "locked" and the molecules simply tumble as approximate spheres. For cationic sandwich complexes the formal charge has little effect on T_1. Ion pairing in CpM derivatives is also explored using relaxation data.

Introduction

Spin-lattice relaxation times (T_1) have been used increasingly as a tool for investigating molecular dynamics of solutions. Several recent reviews [1–3] are available which reveal some confusion in the notation and nomenclature used in the underlying theory of relaxation processes. This problem has been addressed by Lambert et al. [3]. The confusion has been compounded by the use of SI units by some authors and cgs units by others. The former are used throughout this work. Practical details of T_1 measurements have also recently appeared [4]. Although much attention has been devoted to ^{13}C relaxation times of organic molecules, relatively little work has been done in organometallic systems. Sandwich complexes are particularly suitable cases for study since it is possible to analyse the molecular motions in terms of both overall tumbling and ring rotation thus enabling the estimation of rotational barriers of the carbocyclic ligands.

The theory of spin-lattice relaxation of molecules undergoing such anisotropic reorientation has been set out by Woessner [5] and subsequently developed by Wallach [6] and Allerhand [7,8] amongst others. The basis of the theory can be found in Abragam's [9] book on nuclear magnetism. The first use of NMR spectroscopy in the determination of rotational barriers in sandwich complexes was as early as 1957 by Fischer, Rochow and Mulay [10] who used ^1H NMR linewidths and second moments to estimate the rotational barriers in ferrocene. However, it

0022-328X/91/$03.50

was not until the advent of FT techniques that detailed relaxation studies on ^1H and particularly ^{13}C nuclei could be made. The first report of T_1 measurements on ferrocene derivatives appeared in 1972 [11] and outlined the overall strategy for separating ring spin from molecular tumbling. This methodology has since been recently elaborated by Mann's group who succeeded in calculating rotational barriers for a number of ferrocene [12] and rhodium and iridium [13] sandwiches. In addition, barriers to rotation of cyclopentadienyl ligands in the solid phase have been measured using ^1H spin-lattice relaxation [14,15]. We report here relaxation data for a range of ferrocene derivatives and other related sandwich compounds and illustrate their use in elaborating the molecular dynamics of these systems.

Methodology

The two most commonly encountered mechanisms for spin-lattice relaxation are the dipole–dipole (DD) mode and the spin rotation (SR) mode. The latter dominates in small molecules such as cyclopropanes but gradually gives way to dipole–dipole relaxation as the size increases, such that for cyclohexanes the DD mode becomes dominant [16]. The DD contribution to relaxation can be determined from the Nuclear Overhauser factor (NOE) which has a value close to 2 for ^{13}C nuclei in cases where only the DD mechanism is operating. The relaxation time for this process ($T_{1\mathrm{DD}}$, hereafter simply referred to as T_1) is given by the equation

$$T_{1\mathrm{DD}} = T_1^{\mathrm{obs}} 1.988(\mathrm{NOE})^{-1} \tag{1}$$

The most effective DD relaxation occurs under the extreme "narrowing" condition $\omega_0\tau_c \ll 1$ where ω_0 is the Larmor frequency and τ_c the correlation time for molecular tumbling. For ^{13}C relaxation, τ_c itself is related to T_1 via the relationship

$$T_1^{-1} = \frac{\mu_0^2 \gamma_H^2 \gamma_C^2 \hbar^2 S(S+1)\tau_c}{12\pi^2 r_{CH}^6} \tag{2}$$

where μ_0 is the permeability of a vacuum, γ_H, γ_C are the gyromagnetic ratios for H and C nuclei, S is the proton spin quantum number and r_{CH} is the carbon–hydrogen bond length associated with the carbon nucleus under investigation. Using values for μ_0 in SI units and $S = \frac{1}{2}$, eq. 2 reduces to

$$T_1^{-1} = \frac{10^{-14}\gamma_H^2 \gamma_C^2 \hbar^2}{r_{CH}^6}\tau_c \tag{3}$$

which for ferrocene (FcH) [$r_{CH} = 1.104 \times 10^{-10}$ m] [17] yields the equation

$$T_1^{-1}(\mathrm{FcH}) = 1.989 \times 10^{10}\tau_c \tag{4}$$

For isotropic tumblers, τ_C can be calculated from the Stokes–Einstein based equation [18]

$$\tau_C = \frac{4\pi a^3 \eta \mathrm{f}(r)}{3kT} \tag{5}$$

where a is the molecular radius of the tumbler, η solvent viscosity and $\mathrm{f}(r)$ is a microviscosity correction factor which is commonly held to have a value of approximately 0.16 for pure liquids. Ferrocene is almost an ideal molecule for testing

Table 1

^{13}C Relaxation times (T_1, s) for some substituted ferrocenes $(C_5H_4X)Fe(C_5H_4Y)$

X	Y	Solvent	Concentration (M)	T_1				
				C1	C2	C3	Cp	Others [a]
H	H	$CDCl_3$	0.1	13.8	–	–	–	–
H	H	C_6H_5D	0.1	16.3	–	–	–	–
H	H	C_6D_6 [b]	– [c]	14.3				
H	H	DMSO-d_6	0.1	7.4	–	–	–	–
H	H	acetone-d_6	0.1	11.7	–	–	–	–
n-C_4H_9	H	C_6H_5D	0.1	–	4.0	4.6	10.2	side chain C1′ 4.6, C2′ 3.4, C3′ 4.0, C4′ 5.7
n-C_4H_9	H	C_6D_6 (38°) [b]	– [c]	– [c]	2.5	2.6	6.0	side chain C1′ 2.0, C2′ 2.0, C3′ 2.8, C4′ 3.6
n-C_4H_9	H	$C_6D_5CD_3$ [d]	0.8	– [c]	6.1	6.4	10.5	[c]
t-C_5H_{11}	H	C_6H_5D	1.9	– [c]	4.5	4.5	8.0	C1′ 2.6, C3′ 3.3, *gem* dimethyl 2.0
t-C_5H_{11}	H	$C_6D_5CD_3$ [d]	0.8	– [c]	6.8	6.3	10.5	[c]
n-$C_{16}H_{33}$	H	C_6H_5D	0.4	~ 37	3.2	4.0	6.7	C1′ 3.1′ C2′ 2.8, C14′ 2.9, C15′ 3.8, C16′ 5.1
Ph_3C	H	$CDCl_3$	0.24	7.9	1.5	1.0	2.3	phenyl carbons C1′ 21.3, C2′ 1.29, C3′ 1.45, C4′ 1.25
CH_3CO	H	C_6D_6 [b]	– [c]	– [c]	3.2	3.2	6.2	CH_3 7.9
CH_3	CH_3	acetone-d_6	0.43	23	13.3	12.1	–	Me 8.3
Ph_3C	Ph_3C	$CDCl_3$	0.05	–	0.49	0.57	–	phenyl carbons C1′ 7.2, C2′ 0.73, C3′ 0.58, C4′ 0.90

[a] Side chains numbered in conventional manner. [b] Data from ref. 11. [c] Not reported. [d] Data from ref. 12 interpolated at 31° C.

this theory since it closely approximates to a sphere. Thus using equations 4 and 5, a value for T_1 can be calculated. This assumes, of course, that the DD mechanism is dominant. Evidence that this is indeed so comes from the observed high NOE values [11,12]. A question arises as to the correct value of a to be used in such calculations. If a is taken as simply the Fe–H distance (2.86×10^{-10} m) [17] then for solvent $CDCl_3$ at 30 °C a T_1 of about 26 s is calculated. However, if the Van der Waal's radius for hydrogen is included, a value of about 10 s is found which is much closer to the observed T_1 of 13.8 s (Table 1). From these rather simple calculations it therefore appears that ferrocene can indeed be regarded as an isotropic tumbler.

Many molecules not only tumble but also possess groups which can undergo internal rotation. One of the simplest cases in organic molecules is that of a methyl group. Much effort has been devoted to the dissection of the motions of such anisotropic tumblers into overall molecular tumbling (correlation time τ_c) and internal reorientation or rotation (τ_m).

The following equations have been developed from Woessner's original work [5]:

$$\chi = \frac{T_1(\text{anchor})}{T_1(\text{rotor})} = \tfrac{1}{4}(3\cos^2\theta - 1)^2 + 18(5+\rho)^{-1}\sin^2\theta\cos^2\theta + \tfrac{9}{4}(1+2\rho)^{-1}\sin^4\theta \tag{6}$$

where θ is the angle between the rotational axis and the C–H bond and

$$\rho = (\tau_c + \tau_m)/\tau_m \tag{7}$$

The basic premise is that the non-rotating part of the molecule is "anchored" in the solvent leaving the rotor free to spin. For ferrocene, θ can be approximated to 90° and a combination of eq. 6 and 7 gives

$$R_\tau = \tau_m/\tau_c = (4\chi - 1)/6(1-\chi) \tag{8}$$

from which the relative rates of spinning and tumbling can be evaluated.

Results and discussion

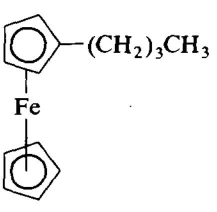
Tables 1 and 2 list the T_1 data for a series of ferrocenes. The results for ferrocene itself clearly show the effect of viscosity on T_1, the lowest value being found in the most viscous medium (DMSO). For the mono-substituted ferrocenes the substituted cyclopentadienyl (Cp) ring is considered as the anchor and the free Cp as the rotor. Our T_1 values (in benzene-d_1) for n-butylferrocene compare reasonable well with those of Mann [12] in toluene-d_8 but are higher than those of Levy [11] in

Table 2

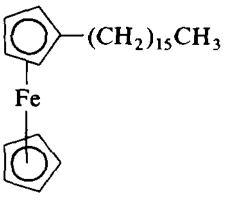
^{13}C Relaxation times (T_1, s) for bridged ferrocenes in $CDCl_3$

Bridge	Concentration (M)	C1	C2	C3	Cα	Cβ	Cγ
α β $-CH_2-CH_2CH_2$	0.39	–	9.5	6.1	5.1	4.7	–
α β γ $-CO-CH_2-CH_2$	0.55	17.1	5.2	4.5	–	4.4	3.3

benzene-d_6 which suggests that degassing in the latter work was not complete. The T_1 values of the CH_2 groups are almost identical to those in the $(CH_2)_3$ bridge in the [3] ferrocenophanes (Tables 2). The latter should again approximate to an isotropic tumbler. This gives added support to the concept of the "anchor" group acting just as a tumbler. The presence of a long chain substituent (as in hexadecylferrocene) should provide a more secure anchor. The T_1's for C2 and C3 however are almost identical to those in n-butylferrocene. It is instructive to compare values of $R_\tau = \tau_m/\tau_c$ (from eq. 8) for the series of monosubstituted ferrocenes.



$R_\tau = 0.20$



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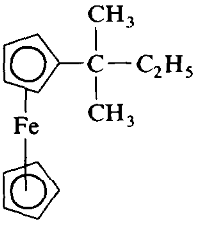

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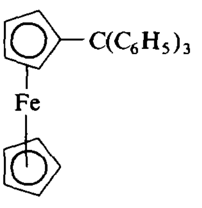
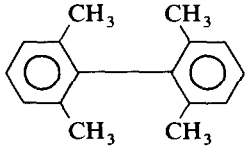
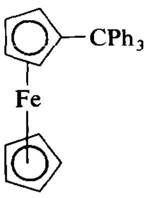


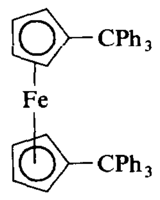
0.43

For complete inhibition of rotation of the free Cp ligand R_τ should be unity. As expected, as the bulk of the side chain increases higher values of R_τ occur but even with the extremely bulky triphenylmethyl (trityl) substituent a value of unity is not approached. A barrier of 35.1 kJ mol^{-1} has been found for the rotation of the free Cp ring in t-butylferrocene [19] which should be approximately the same as that in t-pentylferrocene. This value, however, was obtained from solid state measurements and may well be substantially lower for the solution phase, as shown for t-pentylferrocene where a barrier of 8.6 kJ mol^{-1} has been reported [12]. Molecular models indicate that the barrier for tritylferrocene should be much greater. The R_τ values however are very similar. One possible explanation of this anomaly is that in such sterically crowded systems, the motion of the Cp ring is not one of rotation but of a "tick-tock" type. Further evidence of steric forces at work in the trityl derivative comes from an analysis of the *ortho/meta* carbon relaxation times compared with that of the *para* carbon in the phenyl groups. Preferential reorientation about the C1–C4 axis causes the *ortho* and *meta* carbons (off the axis) to relax at a significantly slower rate than the *para* carbon [20]. Thus the ratio $T_1^{o,m}/T_1^p$ gives a measure of the rotation about this axis. If no rotation occurs then the ratio becomes unity. The following series,

CH_3Ph $HCPh_3$ PPh_3







$\frac{T_1^{o,m}}{T_1^p} = 1.37$ 1.55 1.30 1.11 1.10 0.73

clearly shows the lack of rotations of the phenyl groups in the tritylferrocenes compared with the value of 1.1 for 2,2′,6,6′-tetramethylbiphenyl where restricted

Table 3

^{13}C Relaxation times (T_1, s) for some metal sandwich complexes at 304 K

Complex	Solvent	T_1				
		Concentration (*M*)	Cp	Arene		Other
$[C_6H_6FeC_5H_5]^{+}$ [a]	$(CD_3)_2CO$	0.26	9.9		9.3	–
	$(CD_3)_2SO$	0.1	2.7		2.3	–
	$(CD_3)_2SO$ [b]	0.1	4.4		4.7	–
$[(C_6H_5Me)FeC_5H_5]^{+}$ [a]	$(CD_3)_2CO$	0.26	10.5	C2	6.5	–
				C3	6.4	–
				C4	5.8	–
$[(C_6Me_6)FeC_5H_5]^{+}$ [a]	$(CD_3)_2CO$	0.16	8.9		61	9.1 (Me)
$[(C_6Me_6)_2Fe]^{2+}$ [a]	$(CD_3)NO_2$	0.065	–		17.8	5.4 (Me)
$[(C_5H_5)_2Co]^{+}$ [a]	$(CD_3)_2CO$	0.14	13.0		–	–
$[C_5H_5Fe(CO)_2I]$	$(CD_3)_2CO$	0.1	14.2		–	–
$[C_6H_6Cr(CO)_3]$	$(CD_3)_2CO$	1.0	–		13.6	–
$[(C_6H_5Me)Cr(CO)_3]$	$(CD_3)_2CO$	1.7	–	C1	37	–
				C2	7.8	–
				C3	7.4	–
				C4	7.1	–

[a] PF_6^- salt. [b] At 333 K.

rotation occurs [21]. An additional point to note is that T_1 values for the latter complexes are markedly lower. This is almost certainly due to the increased size of the molecule (eq. 5). Monotritylferrocene has a "radius" of about 6.6×10^{-10} m (estimated from molecular models) which gives a calculated T_1 of 2.1 s which is close to the observed values (1.0–2.3 s). A similar calculation for the bis-(trityl) derivative gives a calculated value of about 0.9 s which again compares reasonably well with those observed (0.49–0.57 s). For both $FcCPh_3$ and $Fc(CPh_3)_2$, the phenyl and Cp carbons have approximately the same T_1 values which should be the case if no internal rotation occurs and the molecule simply tumbles as a sphere.

Table 3 lists T_1 values for a range of transition metal sandwich complexes. Here it is assumed that DD relaxation is dominant. There is evidence for this in that for $[C_6H_6FeCp][PF_6]$ the T_1 increases with temperature rather than decreases as would be the case if the SR mechanism dominated. The T_1 values for the benzene and Cp ligands are almost identical, indicating uniform tumbling and internal rotations. The values are indeed close to those of ferrocene itself. This is true of the other

Table 4

^{13}C Relaxation times for free aromatic ligands in $CDCl_3$

Arene	Concentration (*M*)	C1	C2	C3	C4	Others
Benzene	0.2	19.8	–	–	–	–
Mesitylene	0.2	39.0	7.8	–	–	–
Hexamethylbenzene	1.14	67.8	–	–	–	Me 11.9
Triphenylmethane	0.89	25.4	2.9	3.0	1.9	CH 3.0
Triphenylphosphine	0.1	–	2.7	2.5	2.0	–

Table 5

^{13}C Relaxation times (T_1, s) for cyclopentadienyl derivatives (MCp) of alkali metals in solvent tetrahydrofuran

MCp	Concentration (M)	T_1
LiCp	1.0	5.2
	2.0	3.2
NaCp	0.5	3.5
	0.5 [a]	2.6
	1.0	2.2
	1.0 [a]	3.0
	2.0	1.1
	2.0 [a]	2.8

[a] One equivalent of 18-crown-6 added.

sandwiches $[Cp_2Co][PF_6]$, $CpFe(CO)_2I$, $C_6H_6Cr(CO)_3$. Charge on the central metal atom therefore has little effect. Complexation of the ligand causes a uniform decrease in T_1 compared to that of the free ligand (Table 4) which again is probably due to size factors. For $[C_6H_5CH_3FeCp][PF_6]$ and $(C_6H_5CH_3)Cr(CO)_3$ of the *ortho, meta* and *para* T_1 values were identical within experimental error as anticipated for a complexed arene where no rotation is allowed about the C_1– C_4 axis. For the $[ArFeCp]^+$ series the T_1 values for the Cp ligand do not vary appreciably across the series: Ar = C_6H_6, C_6H_5Me, C_6Me_6 showing that even in the hexamethylbenzene complex the Cp is freely rotating. By contrast the T_1 values for the quaternary carbons in $(\eta^6\text{-}C_6Me_6)_2Fe^{2+}$ are much lower than those of $(\eta^6\text{-}C_6Me_6)(\eta^5\text{-}Cp)Fe^+$ suggesting restricted rotation in the former. The dominant relaxation mechanism operating in this instance is probably that of spin rotation.

T_1 values were obtained for alkali metal cyclopentadienides in THF (Table 5). Both the Li and Na derivatives showed a marked concentration dependence which we attribute to changes in ion pair concentrations [22]. Addition of the crown ether, 18-crown-6, (which specifically complexes Na^+) to the NaCp solutions removes the concentration dependence which offers strong support for the above explanation. Both ^7Li and ^{23}Na have quadrupole moments which could enhance the relaxation of the ^{13}C nuclei in the Cp^-. The effect will clearly be distance-related so that the more intimate the ion pair the more efficient is the quadrupole relaxation. The crown ether has the effect of separating the two ions thus reducing this effect. It is noticeable that the actual values of T_1 are much smaller than those of other Cp complexes which again suggests the operation of another relaxation mechanism. It should also be recalled that for small molecules the spin rotation mode can become important.

Experimental

Ferrocene, n-butylferrocene, t-pentylferrocene, dimethylferrocene, $[(C_5H_5)_2Co][PF_6^-]$, $C_5H_5Fe(CO)_2I$, $C_6H_6Cr(CO)_3$, $(C_6H_5CH_3)Cr(CO)_3$, C_5H_5Li and C_5H_5Na were purchased from Aldrich Chemical Co. Ltd. and recrystallised (where appropriate) prior to use. The $(\eta^6$-arene$)(\eta^5$-cyclopentadienyl)iron(II) salts [22]

($ArFe^+Cp$), bis(η^6-arene)iron(II) salts [24], mono and 1,1′-bistriphenylmethyl ferrocenes [25] and [3]-ferrocenophanes [26,27] were synthesised by established routes.

^{13}C NMR spectra and relaxation times (T_1) were obtained using a Bruker WP 80SY spectrometer. ^{13}C assignments were previously available for most derivatives (for ferrocenes see ref. 28, for $ArFe^+Cp$ complexes see ref. 23).

T_l *measurements*

Sample solutions were thoroughly degassed prior to use by passing dry, oxygen-free N_2 through the solutions for 15 min then tightly stoppering the tube. T_1 values were obtained using the inversion recovery technique at a probe temperature of 304 K using a delay of at least 8 T_1 s. Solution volumes were kept constant at 2.5 ml and the same tube was used throughout. In some cases the FID decay was treated by the Guggenheim method [29] which does not require a knowledge of the final peak intensities provided the process is truly first order. In these cases the T_1 values obtained closely agree with those obtained by the conventional method. The reproducibility under these conditions was ±5% as determined from five separate measurements on ferrocene in $CDCl_3$.

Acknowledgement

The authors wish to thank Dr.B.E. Mann (University of Sheffield) for helpful discussions.

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