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^{57}Fe Spin-lattice Relaxation Time of Fe(CO)$_5$ and Ferrocene

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Synopsis. Spin-lattice relaxation times (T_1's) of ^{57}Fe were determined by the inversion recovery method to be 80 (± 10) s at 293 K and 4 (± 1) s at 303 K for Fe(CO)$_5$ and ferrocene, respectively. Predominant relaxation mechanisms were considered to be chemical shift anisotropy and spin-rotation for the former and the latter complexes, respectively.

Although chemical shifts of ^{57}Fe NMR of many iron complexes have been determined by a combination of pulse FT techniques with large sample tubes and a high magnetic field,[1)] little has been known about the relaxation processes, which are important to understand the molecular dynamics of the complexes. ^{57}Fe nucleus with nuclear spin of one half and low natural abundance was believed to have a long relaxation time. Recently we have succeeded in determining the spin-lattice relaxation times of Fe(CO)$_5$ (pentacarbonyliron(0)), and ferrocene (bis(η-cyclopentadienyl)iron(II)). The relaxation time of ferrocene was fairly short as compared with that of Fe(CO)$_5$. Possible relaxation mechanisms to explain these results are discussed.

Experimental

Materials. Fe(CO)$_5$ was purchased from Strem Chemicals, Inc. Ferrocene was obtained from Wako Chemicals, Inc. as a guaranteed grade reagent and purified by recrystallization from benzene. Benzene-d_6 was purchased from E. Merck Japan Ltd.

Measurements. The NMR spectra of ^{57}Fe were measured with a Bruker CXP-300 FT-NMR spectrometer. The static field $B_0 = 7.05$ T (corresponding to a 300 MHz proton Larmor frequency) gave resonance frequencies around 9.7 MHz for the ^{57}Fe nuclei, and was internally locked on a ^{2}H signal of solvent, except for Fe(CO)$_5$ which was measured as neat liquid without lock. The 90° pulse width was determined to be 180 μs, which afforded a H_1 field of 10.1×10^{-4} T. A Bruker temperature controller (B-VT-1000) was employed and calibrated by measuring the proton frequency differences between the resonances of ethyl alcohol.[2)] The NMR spectra of ^{57}Fe for neat Fe(CO)$_5$ and ferrocene in benzene-d_6 solution (1 mol dm^{-3}) were measured at 293 and 303 K at its natural abundance with a sample tube of 15 mm diameter. The ferrocene solution was degassed before the NMR measurements.

Results and Discussion

Fe(CO)$_5$ and ferrocene gave NMR signals at 9.71568 and 9.73056 MHz, respectively. The ratios of these values to the resonance frequency of GeCl$_4$ (ν(Fe)/ν(Ge)) were 0.928155 and 0.929576 which coincide well with the values in the reference,[1)] 0.92815542 and 0.9295803. The half linewidths of the NMR signals were 1.0 and 2.6 Hz for Fe(CO)$_5$ and ferrocene, respectively.

Measurements of spin-lattice relaxation times were achieved by the inversion recovery method combined with a Fourier transform (IRFT). Since the spin-lattice relaxation time, T_1, for the ^{57}Fe NMR of Fe(CO)$_5$ was expected to be around 100 s, the recycle time was taken to be 800 s. The results are shown in Fig. 1. The plot of $-\ln((A_\infty - A_\tau)/2A_\infty)$ *versus* τ, where A_τ and A_∞ are the amplitude of the NMR signal partially relaxed for an inter-pulse time τ, and the amplitude at thermal equilibrium, yielded a T_1 value of 80 (± 10) s.

The partially relaxed NMR spectra for ferrocene in benzene-d_6 solution are shown in Fig. 2. The plot of $-\ln((A_\infty - A_\tau)/2A_\infty)$ *versus* τ gave a T_1 value of 4 (± 1) s.

Since no abundant spin is present in Fe(CO)$_5$, the only possible ways of relaxation are the spin-rotation and/or the chemical shift anisotropy mechanism.[3)] Hence, it is reasonable for the system to have a spin-lattice relaxation time as long as 80 s.

Ferrocene in benzene-d_6 solution had a spin-lattice relaxation time much shorter than that of Fe(CO)$_5$, the reasons for this are now discussed.

In order to determine the rotational correlation time of ferrocene, the spin-lattice relaxation time of the ^{13}C nucleus of ferrocene was measured for the same solution for which the T_1 values of the ^{57}Fe nucleus had been determined. The T_1 values for the ^{13}C nucleus of ferrocene were 12.3 and 10.0 s at 303 and 293 K, respectively, which are in reasonable agreement with the reference values[4)] (14.3 s at 311 K). The ^{13}C nucleus directly bound with one or more proton(s) is relaxed predominantly through the dipolar mechanism.[5)] Hence the ^{13}C nucleus of ferrocene is presumed to be relaxed by

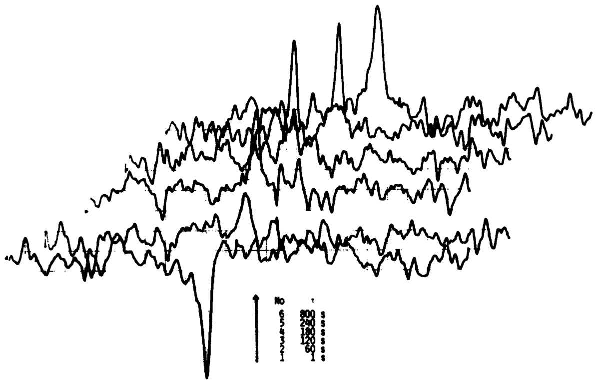

Fig. 1. The partially relaxed ^{57}Fe NMR spectra for Fe(CO)$_5$. The duration of 90° pulse was 180 μs at a transmitter gain with peak to peak voltage of 200 V. The recycle time was 800 s. The inter-pulse time (τ) values were 1, 60, 120, 180, 240, and 800 s from the bottom to the top spectra. Sweep width: 100 Hz, memory size: 8×10^3 words, line-broadening: 1 Hz, number of transients: 52, temperature: 293 K.

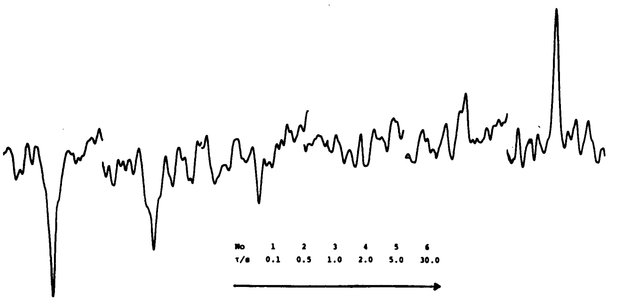

Fig. 2. The partially relaxed ^{57}Fe NMR spectra for ferrocene in benzene-d_6 solution (1 mol dm^{-3}). The duration of 90° pulse was 180 μs at a transmitter gain with peak to peak voltage of 200 V. The recycle time was 30 s. The inter-pulse time (τ) values were 0.1, 0.5, 1.0, 2.0, 5.0, and 30 s. Sweep width: 150 Hz, memory size: 8×10^3 words, linebroadening: 1 Hz, number of transients: 520, temperature: 303 K.

the dipole (^{57}Fe) and dipole (^{1}H) interaction mechanisms. The spin-lattice relaxation time for the dipolar interaction mechanism, $T_1{}^{\mathrm{dd}}$, for a nucleus I being relaxed by a nucleus S under the extreme narrowing conditions can be written as$^{6)}$

$$1/T_1{}^{\mathrm{dd}} = (\mu_0^2\gamma_{\mathrm{I}}^2\gamma_{\mathrm{S}}^2\hbar^2/12\pi^2)S(S+1)\Sigma(1/r^6)\tau_r, \tag{1}$$

where μ_0, γ, S, r, and τ_r are magnetic permeability in vacuum, magnetogyric ratio, spin quantum number for the nucleus S, distance between the nuclei I and S, and a rotational correlation time, respectively. Taking the above experimental T_1 value as the $T_1{}^{\mathrm{dd}}$, and using Eq. 1 and the bond distance (1.095 Å) between ^{13}C and ^{1}H,$^{7)}$ we can calculate the rotational correlation time, τ_r, to be 3.0×10^{-12} s at 303 K. Under the assumption that the ^{57}Fe nucleus of ferrocene has a rotational correlation time similar to that for the ^{13}C nucleus, and that the ^{57}Fe nucleus is relaxed by the dipolar mechanism, the spin-lattice relaxation time of the ^{57}Fe nucleus was calculated to be 2.2×10^4 s from Eq. 1 and the structure of ferrocene.$^{7)}$ This value, which is far from the experimentally observed one (4 s), therefore, indicates that other relaxation mechanisms should be considered for the relaxation of the ^{57}Fe nucleus in ferrocene.

The spin-lattice relaxation time for the chemical shift anisotropy mechanism ($T_1{}^{\mathrm{CA}}$) can be expressed by

$$1/T_1{}^{\mathrm{CA}} = (2/15)\gamma_{\mathrm{I}}^2H_0^2\Delta\sigma^2\tau_r, \tag{2}$$

under the extreme narrowing condition.$^{8)}$ The chemical shift anisotropy ($\Delta\sigma$) necessary to explain the observed T_1 value (4 s) was calculated to be 2.0×10^4 ppm, under the assumption that the rotational correlation time, τ_r, for the ^{57}Fe nucleus is similar to that determined for the ^{13}C nucleus. This value appears to be one order of magnitude too large as compared with $\Delta\sigma$ values experimentally determined for other metallocenes (*e.g.*, 6400 ppm for $[\mathrm{Co^{III}(C_5H_5)_2}]\mathrm{NO_3}$$^{9)}$). Therefore the relaxation of the ^{57}Fe nucleus in ferrocene can not be explained by the chemical shift anisotropy mechanism only. Accordingly another relaxation mechanism, *i.e.*, spin-rotation mechanism, will play an important role in the relaxation of ^{57}Fe nucleus. The temperature dependence of the ^{57}Fe relaxation time of ferrocene which showed a longer value at lower temperature (5 s at 293 K) supported this conclusion.$^{7)}$

For the relaxation of the ^{13}C nucleus of $\mathrm{Fe(CO)_5}$, it was reported that the chemical shift anisotropy was the predominant mechanism and that the rotational correlation time τ_r was 5×10^{-12} s at 293 K.$^{3)}$ By use of this correlation time for the ^{57}Fe nuclei of $\mathrm{Fe(CO)_5}$, the chemical shift anisotropy necessary to explain the experimental T_1 value (80 s) was calculated to be 4000 ppm from Eq. 2. Although this value is somewhat larger than that observed for other metal carbonyls ($\Delta\sigma=1400$ ppm for $[\mathrm{Mn(CO)_5Cl}]$$^{10)}$), the chemical shift anisotropy mechanism will be predominant in the relaxation for the ^{57}Fe NMR of $\mathrm{Fe(CO)_5}$.

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