Oxygen-17 Relaxation Times of Metallocarbonyls: the Use of the ^{17}O Electric Quadrupole Coupling as a New Structural Probe

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The ^{17}O spin–lattice relaxation times at 54.25 MHz for seven selected metallocarbonyls are in the range 8 to 50 ms at 298 K; the variations are dependent upon the molecular size, the transition metal, and the stereochemical position of the CO group, and may be interpreted in terms of variation of ^{17}O electric quadrupole coupling constants which show stereochemical dependence, when the effects of correlation times have been allowed for.

In the last decade ^{13}C n.m.r. spectroscopy has considerably increased our knowledge of metallocarbonyls *e.g.* their solution structures and dynamic behaviour.[1,2] In contrast to organic cases, however, measurements of ^{13}C T_1 values of organometallic complexes have received only limited attention despite their general potential for structural and motional studies. In the case of the CO groups of metallocarbonyls this deficiency can be ascribed partly to the long T_1 values (up to 200 s at 2.1 T) which render measurements very time consuming. More importantly there is the considerable difficulty of factorizing the relaxation behaviour into various contributions arising from the different interactions, such as the spin rotation and chemical shift anisotropy mechanisms.[3]

We demonstrate here that both these limitations can be overcome for metallocarbonyls by the use of ^{17}O n.m.r. spectroscopy. Even at the low natural abundance level for ^{17}O (0.037%), good spectra can be produced quickly because the relatively short ^{17}O relaxation times (measured here to be in the region of 10 ms) allow rapid pulsing to be used in accumulations without the production of saturation. Secondly, the ^{17}O lines are quite narrow and well resolved.[4–6] Thirdly, the ^{17}O T_1 relaxation times are dominated by *one* mechanism, *viz.* the electric quadrupolar.[7] They are therefore easier to interpret in principle than ^{13}C T_1 values.

In the extreme narrowing region and for isotropic motion, the electric quadrupolar relaxation rate for ^{17}O ($I = 5/2$, $Q = -2.6 \times 10^{-26}\,\mathrm{cm}^2$) is given by equation (1),[7] where

$$\frac{1}{T_1} = \frac{3}{125}\left(\frac{e^2qQ}{\hbar}\right)^2\left(1 + \frac{\eta^2}{3}\right)\tau_c \qquad (1)$$

e^2qQ/h is the electric quadrupolar coupling constant (QCC), τ_c is the correlation time for molecular reorientation, and η is the asymmetry factor, which for the axially symmetric terminal CO groups considered here is zero. There are therefore only two variables which need to be considered: QCC and τ_c.

Approximate estimates of τ_c for isotropic tumbling may be made by application of the Stokes-Debye formula,[8] equation (2), where η' = viscosity, v = molecular volume, f = micro-viscosity factor (0.16), k = Boltzmann's constant, and T is the absolute temperature. This equation may be tested for metallocarbonyls against the published measurement of τ_c for $Fe(CO)_5$ derived from ^{13}C n.m.r. studies of the pure liquid.[3] In the temperature interval 253—313 K the range for τ_c is 3.5—9.0 ps. Application of equation (2) to $Fe(CO)_5$ in solution in toluene at 298 K gives a value for τ_c of 4.6 ps. The good agreement lends credence to the applicability of equation (2) to other metallocarbonyl derivatives.

$$\tau_c = \frac{\eta' v f}{kT} \qquad (2)$$

The ^{17}O T_1 values given in Table 1 were obtained on a Bruker WH-400 spectrometer at 54.25 MHz and 9.4 T by use of the inversion recovery technique.[9] It can be seen from Table 1 that part of the variation in the T_1 values arises from changes in τ_c from molecule to molecule but that the remaining intermolecular variation is definitely attributable to the ^{17}O QCC values. The observation of *intra*molecular variations in the T_1 values is a most important result since it enables ratios of QCC values to be deduced for each molecule even without a knowledge of τ_c, provided the motion is isotropic and there is only one τ_c for each molecule. The T_1 results for the isostructural $M_2(CO)_{10}$ (M = Mn, Re) cases are particularly interesting since they allow a test for anisotropic motion. There are two possible motions of this type: (i) anisotropy in the overall tumbling and (ii) internal rotation about the metal–metal bond which should presumably be easier for M = Re than for M = Mn. From published structural data[10,11] one can calculate that $Re_2(CO)_{10}$ is a prolate symmetric top and that the moment of inertia I_A (along the Re–Re bond) is about 13% smaller than $I_B(=I_C)$. The axes of preferred overall motion and internal motion are thus collinear. The effect of each of these motions should be to shorten the τ_c value for the equatorial CO groups relative to the value for the axial CO groups, and should therefore make ^{17}O T_1 (equatorial) $> T_1$ (axial). *In fact the opposite is true*, and the simplest conclusion is that the motion is in fact isotropic. The dominant variable therefore governing the relaxation times is QCC. The intramolecular difference between the ^{17}O T_1 values persists in $Mn_2(CO)_{10}$ and is in the same sense as for M = Re, although it is not as large. These results taken together are consistent with (i) isotropic motion and (ii) a structural effect on QCC such that the value of the ^{17}O QCC for an axial CO (*trans* to a metal–metal bond) is smaller than for an equatorial CO (*trans* to another CO).[12]

Table 1

Compound[a]		^{17}O Shift/p.p.m.[b]	T_1/ms[c]	τ_c/ps	QCC/MHz
I	$Fe(CO)_5$	383.6	50	4.6	2.13
II	$Mn_2(CO)_{10}$	367.9 (1)	23.4	7.6	2.43
		387.0 (4)	15.2		3.02
III	$Re_2(CO)_{10}$	337.0 (1)	29.4	8.0	2.18
		370.5 (4)	13.2		3.24
IV	$Rh_2(CO)_4Cl_2$	341.1	19.7	5.0	3.27
V	$H_2Os_3(CO)_{10}$	333.6 (2)	16.1	8.5	2.76
		346.5 (4)	23.6		2.29
		357.5 (2)	17.7		2.64
		358.4 (2)	20.7		2.45
VI	$Br_2Os_3(CO)_{12}$	330.1 (2)	8.8	11.5	3.23
		340.3 (2)	21.4		2.07
		359.2 (4)	10.2		3.00
		369.2 (4)	8.1		3.27

[a] Solvent $CDCl_3$ except for I which was measured in toluene. [b] Relative to H_2O; relative intensities of peaks are given in brackets. [c] Measured at 54.25 MHz and 298 K.

The case for isotropic tumbling is strengthened by the results for VI (Table 1) which has a linear metal framework and unique axial CO groups *trans* to Os–Os bonds on the long axis. Anisotropic rotation with preference for rotation around the metal axis should shorten the T_1 values for these groups preferentially. In fact no one T_1 value is uniquely short.

The QCC values in Table 1 deduced by use of the τ_c values obtained from equation (2), vary from 2.12 to 3.27 MHz. These are considerably smaller than values measured for organic carbonyl groups which are in the range 6 to 12 MHz.[13,14] Since T_1 = *ca.* T_2 under extreme narrowing conditions, the relatively long ^{17}O T_1 values for the metallocarbonyls explain their unusually narrow ^{17}O lines and well resolved spectra as previously suggested.[4] Measurement of T_1 from line widths is not reliable however since we note that this method gives some large discrepancies from the values reported in Table 1.

A most interesting result is that the values for QCC are smaller even than the value (4.34 MHz) for carbon monoxide as a free ligand.[15] This establishes that the electric field gradients at the oxygen atoms in the complexes are smaller than the gradient in free CO. The implication is that there is an increased electron density at oxygen in the complexes relative to CO. Metal to ligand backbonding must be partially responsible together with the possibility of less σ-electron withdrawal from the carbon into the M–C σ-bond relative to the carbon lone pair in free CO. Whatever the theoretical rationalisation for the low values for QCC in the metallocarbonyls, however, it is clear that the values may be related in an empirical way to structural factors. This newly discovered structural dependence of the ^{17}O QCC values in metallocarbonyls establishes this type of coupling as a potentially important addition to the organometallic chemist's armoury of ^{13}C and ^{17}O chemical shifts and spin–spin coupling constants.

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