Oxygen-17 and Carbon-13 Relaxation Studies of Metal Carbonyls: Improved Determination of ^{17}O Electric Quadrupole Couplings

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Rotational correlation times for six organometallic carbonyl complexes have been measured by ^{13}C spin–lattice relaxation time and ^{13}C-$\{^1H\}$ nuclear Overhauser enhancement measurements of the organic ligands. Oxygen-17 T_1 n.m.r. measurements on the carbonyl groups yielded the ^{17}O electric quadrupole-coupling constants. The values show structural variation and so could be useful in the assignment of ^{17}O resonances.

Recently several reports dealing with the observation of ^{17}O n.m.r. spectra of metal carbonyl complexes have appeared, showing that this spectroscopic method can be useful for structural studies of this class of compounds.[1,2] A remarkable feature of these spectra is the small width of the ^{17}O resonances compared with the large linewidths observed for organic compounds. This advantage allowed us to study [3] the dynamic behaviour of $[Co_4(CO)_{12}]$ for which previous ^{13}C studies had failed to show the correct solution structure, probably because of rapid ^{13}C relaxation induced by the quadrupolar cobalt nuclei.

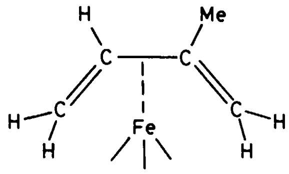
Even though ^{17}O is not a very receptive n.m.r. nucleus (receptivity 1.08×10^{-5} relative to ^1H at natural abundance),[4] the very efficient quadrupolar relaxation allows the use of very short delays between pulses in the accumulation sequence. This permits the acquisition of a large number of transients in a short period of time. The sensitivity enhancement thus gained is of great importance, since it enables measurement of the various relaxation times, T_1, T_2, and $T_{1\rho}$. We believe that these measurements constitute a new valuable tool for probing the structural, electronic, and dynamic properties of this class of molecules in much more detail.[5] The spin–lattice relaxation time, T_1, of a ^{17}O nucleus in the extreme-narrowing region and for isotropic motion of the molecules is given by equation (i), where e^2qQ/h is the nuclear electric quadrupolar

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

coupling constant (q.c.c.), η is the asymmetry factor, and τ_c is the molecular correlation time. If the molecular correlation times are known, this equation provides a method for the calculation of q.c.c. values. Recently we reported the determination of the ^{17}O q.c.c. values for the carbonyl groups of simple metal carbonyls by use of the Stokes–Debye relationship for the estimation of τ_c.[6] It is well known that this approach is only semiquantitative and a better determination of this quantity is needed if more accurate q.c.c. values are to be obtained. In the case of an organometallic carbonyl derivative the overall motional behaviour of the molecule can be determined by the evaluation of the T_1 values for ^{13}C in CH or CH_2 fragments in the organic ligand according to equation (ii), where N is the number of directly bonded hydrogens,

$$\frac{1}{T_1^{DD}} = \frac{N\gamma_C^2\gamma_H^2\hbar^2}{r_{CH}^6}\cdot\tau_c \qquad \text{(ii)}$$

γ_C and γ_H are the gyromagnetic ratios of carbon and hydrogen, r_{CH} is the average C–H bond distance, and T_1^{DD} is the carbon–hydrogen dipole–dipole contribution to T_1 for ^{13}C. This approach, called the dual-spin-probe technique, has already been applied in the case of ^{17}O to the study of 2-pyrrolidone, δ-valerolactam, caprolactam, and ε-caprolactam,[7] as well to study of acetonato-complexes of Be [8] and Al, Ga, and In.[9] We have previously mentioned an application of this technique to the osmium cluster (3), in our investigation [10] of the solution dynamics of the related complex $[Os_3H_2(CO)_{10}]$ by ^{13}C and ^{17}O n.m.r. spectroscopy.



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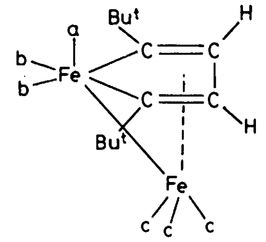

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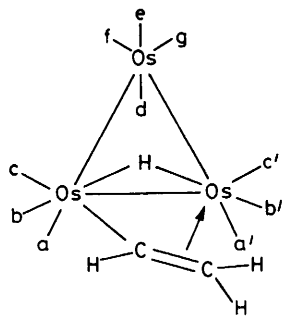

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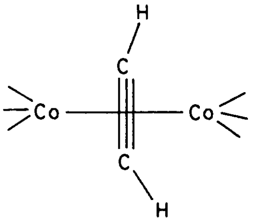

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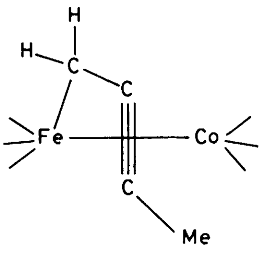

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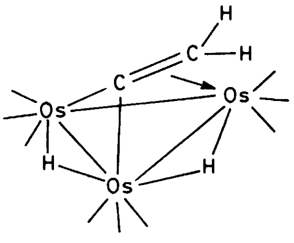

(6)

For this study we have considered six derivatives (1)—(6)

of different metallic nuclearity, for which ^{13}C n.m.r. spectra have already been widely investigated.[11-15] The compounds were chosen also to have a minimum of internal motion in respect of the organic ligand.

Results and Discussion

^{13}C *N.M.R. Results*.—We report in Table 1 the T_1 values for the ^{13}C nuclei of the organic ligands of samples (1)—(6) together with their ^{13}C-{^1H} nuclear Overhauser enhancements (n.O.e.s). In compounds (1) and (3) there are two inequivalent carbon atoms permitting two different estimates of τ_c in each case. For (1) the values are 4.12 and 3.87 ps. The near equality of these values for different carbon centres establishes that the overall molecular tumbling is essentially isotropic. A similar result is found for compound (3) for which the τ_c values are even closer, namely 22.75 and 22.54 ps for the CH and CH_2 groups respectively. In this case, however, a complication is the intramolecular exchange of the vinyl group. Since this can readily be frozen out on the n.m.r. time-scale, the rate constant must be slow enough ($\leqslant 10^5$ s^{-1}) that it can be neglected on the τ_c scale. It is interesting to compare the mean value of τ_c for compound (3), 22.6 ps, with that for (6), 23.0 ps. This comparison shows that the similarity of nuclearity and shape gives almost equal values for τ_c. It is highly likely therefore that the value of 8.5 ps for $[Os_3H_2(CO)_{10}]$ deduced by application[6] of the Stokes–Debye formula is an underestimate. This formula is given in equation (iii), where η' = viscosity, v = molecular volume, f =

$$\tau_c = \eta' v f / kT \qquad \text{(iii)}$$

microviscosity factor, k = Boltzmann's constant, and T is the absolute temperature. One notorious difficulty with expression (iii) is the value to be assigned to f. The value normally taken is 0.16. Although this gave good agreement between the measured and estimated[6] values of τ_c for $[Fe(CO)_5]$, it fails for compound (2) for which it gives an estimate of 6.0 ps compared with the value measured here of 15.7 ps. The measurement of τ_c for (4) proved difficult because the ^{13}C resonances of the acetylene ligand were broadened by the quadrupolar ^{59}Co nuclei ($I = \frac{7}{2}$) and the ^{13}C T_1 values could not be obtained. Rather than using equation (iii) for τ_c we prefer in this case to rely on the close similarity in structure and size between compounds (4) and (5). Since τ_c is measured at 6.85 ps for (5), and we accordingly estimate τ_c for (4) to be slightly smaller at about 6.0 ps because the latter is slightly heavier than compound (5).

^{17}O *N.M.R. Results*.—In Table 2 we report the results for the ^{17}O experiments. For compound (1) the three CO groups are rendered equivalent at 310 K by intramolecular exchange, so that there is no assignment problem.

Table 1. T_1, T_1^{DD}, and molecular reorientation times τ_c for CH and CH_2 fragments

Compound	T_1/s		n.O.e.	T_1^{DD}/s	τ_c/ps
(1)	CH	6.78	1.33	10.13	4.12
	CH_2	4.95	1.83	5.38	3.87
(2)	CH	2.40	1.80	2.65	15.7
(3)	CH	1.38	2.51	1.83	22.75
	CH_2	0.83	2.78	0.92	22.54
(4)	CH	*a*	*a*	*a*	6.0[b]
(5)	CH_2	2.26	1.43	3.04	6.85
(6)	CH_2	0.91	2.99 (max.)	0.91	23.0

[a] Not measured. [b] Estimated, see text.

The assignment of the ^{17}O resonances in compound (2) is straightforward. The single peak of relative intensity 3 at 310 K with a shift of 390.8 p.p.m. corresponds to the $Fe(CO)_3$ unit in fast exchange. When the temperature is decreased this peak broadens, coalesces, and yields at 173 K two peaks of relative intensity 1 : 2 at 429.0 and 371.5 p.p.m. respectively. The high-frequency resonance corresponds to a single CO in a semibridging position and its chemical shift is approximately at the mean value for terminal and symmetrically bridged CO groups.

Partial assignments for compound (3) have been possible since each of the three low-frequency peaks of relative intensity 2 observed at 310 K splits into two signals of intensity 1 at 173 K. The shifts then are: 348.4 and 318.3; 354.0 and 345.7; 343.2 and 339.1 p.p.m. The high-frequency peak at 354.2 p.p.m. (intensity 2) remains unaffected (as in the ^{13}C spectrum) and is therefore assigned to carbonyls f and g which have the same shift since they are remote from the vinyl group and each is *trans* to a metal–metal bond. The peaks at 353.2 and 368.6 p.p.m. arise from the other two carbonyls (d and e) in the $Os(CO)_4$ group, for which we do not have any additional assignment.

In compound (4) each of the two equivalent groups of three carbonyls is in fast exchange as already shown by ^{13}C studies.

The ^{17}O spectrum of compound (5) shows two lines of equal intensity corresponding to two different $M(CO)_3$ groups each in fast local exchange. We assign the peak at 372.3 p.p.m. to the group with M = Fe and the peak at 365.2 p.p.m. to M = Co since the ^{17}O resonances of iron-bound carbonyls are usually to higher frequency than those bound to Co. In addition we note that the low-frequency peak is slightly broader as expected when M = Co. Compound (6) is rigid at room temperature and the assignments cannot be made at this stage.

In general the ^{17}O n.m.r. shifts are in the same order as the ^{13}C shifts for the CO groups. The ^{17}O linewidths are small ($\leqslant$ 50 Hz) and increase as expected on going from the mono- to the tri-nuclear derivatives since τ_c for the overall molecular tumbling increases with increase in the molecular dimensions, and T_2 decreases.

Table 2. Oxygen-17 T_1 and q.c.c. values for CO groups

Compound[a]	^{17}O shift/p.p.m.[b]		T_1/ms[c]	q.c.c./ MHz
(1)		359.9	61	2.08
(2)	a	363.9 (1)	31.3	1.47
	b	357.8 (2)	22.5	1.88
	c	390.8 (3)	22.4	1.88
(3)	a, a′	340.9 (2)	23.4	1.41
	b, b′	345.6 (2)	15.7	1.72
	c, c′	332.6 (2)	20.3	1.52
	d	368.6 (1)	17.4	1.64
	e	353.2 (1)	14.9	1.77
	f, g	354.2 (2)	21.0	1.49
(4)		368.0	19.2	3.04
(5)	$Fe(CO)_3$	372.3	23.3	2.75
	$Co(CO)_3$	365.2	18.3	3.10
(6)		355.9 (1)	10.9	2.05
		354.6 (1)	19.1	1.55
		350.0 (1)	20.1	1.51
		339.8 (1)	43.0	1.03
		334.2 (2)	22.3	1.44
		332.5 (1)	23.9	1.39
		327.0 (1)	22.9	1.42
		324.0 (1)	28.6	1.27

[a] Solvent $CDCl_3$. [b] Relative to water; relative intensities of peaks are given in parentheses. [c] Measured at 54.25 MHz and 310 K.

The variation in the T_1 values for ^{17}O in the compounds reported here is from 10 to 61 ms. This is essentially the same as the range (8—50 ms) reported previously. The larger molecules have the shorter T_1 values, as noted similarly for T_2 above, because of the effect of τ_c. Since the electric quadrupolar mechanism dominates the relaxation behaviour, equation (i) is both applicable and sufficient. The extreme-narrowing condition is satisfied in the experiments reported here and all the evidence suggests that the overall tumbling motion is isotropic. That conclusion of our preliminary study[6] is strongly supported by the results reported here for ^{13}C T_1 values in the rigid organic ligands of compounds (1) and (2).

Although the presence of the relatively large tertiary butyl groups in compound (2) might at first be thought likely to induce some anisotropy into the molecular motion, simple calculation shows that these groups have relatively low mass in comparison to the metallic framework. The isotropic nature of the overall tumbling shows that the τ_c values determined by the ^{13}C n.m.r. work on the rigid organic ligands can also be employed in the ^{17}O case.

There remains the problem of non-rigidity in the carbonyl groups themselves. In complexes (1), (2), (4), and (5), $M(CO_3)$ groups are involved in fast intramolecular exchanges at room temperature. These polytopal rearrangements can readily be frozen out at moderately low temperature and are therefore relatively slow on the τ_c scale. They can therefore be neglected as far as equation (i) is concerned.* T_1 Values measured on peaks which have coalesced will be averaged over the various sites involved, as in compound (3).

It is worth emphasizing, as was remarked previously, that given isotropic overall tumbling, intramolecular variations in T_1 must reflect structural variations in q.c.c. values. Ratios of these values within any one molecule can then be obtained without any knowledge of the τ_c value.

Access to τ_c values allows absolute values of q.c.c. to be obtained and permits intermolecular comparisons.[16] The results for this study are given in Table 2. The asymmetry factor η has been assumed to be zero for terminal M–C–O groups since they have axial symmetry.

These results for metal carbonyl complexes confirm[6] that for the terminal CO groups at least the q.c.c. values are smaller than the previously reported values for free CO (4.43 ± 0.4 MHz)[17] and for carbonyl groups in organic derivatives (*ca.* 6—12 MHz).[18] This fact must be ascribed to the ability of transition metals to back-donate electrons to the CO group by d_π–p_π bonding which reduces the asymmetry of charge at the oxygen atoms, and lowers q.c.c. This ability is not confined to terminally bound CO groups since preliminary results show low q.c.c. values for 'capping' μ_3-CO groups as well.[5]

The variations for the $Fe(CO)_3$ groups in compounds (1), (2), and (5) are considerable, being 2.08, 1.88, and 2.75 MHz respectively, and must reflect subtle bonding differences. The $Co(CO)_3$ groups in (4) and (5) by contrast give nearly equal q.c.c. values since the two bonding situations are similar. The largest intramolecular variation is found in compound (6) for which a factor of 2 is involved. This is larger than for (3) and larger than noted previously:[6] the τ_c values for $[OsH_2(CO)_{10}]$ and $[Os_3Br_2(CO)_{12}]$ appear to be too low, possibly by a factor of 2 or 3, and the q.c.c. values are correspondingly too large.

It is tempting to try to use the q.c.c. values for compound (6) to produce an assignment, if only partial, of the ^{17}O resonances, say for the peaks with the extreme q.c.c. values of 1.03 and 2.05 MHz. Each of these is outside the range of values (1.41—1.77 MHz) for (3). No unique CO groups however can be picked out in the structure of (6) since the relative structural effects on q.c.c. of groups such as bridging hydrogens, σ- and π-bonded organic groups are not yet delineated.

Similarly the effect of variation in the transition metal on q.c.c. is not clear since the ranges of values measured so far overlap for the few metals studied. Thus, for the metals reported here we have: Fe(CO), 1.47—2.75; Os(CO), 1.03—2.05; and for Co(CO), 3.04—3.10 (two values only). Only further study will reveal whether the order Os, Fe, Co is maintained.

In conclusion we can say that the increased availability of multinuclear n.m.r. spectrometers will contribute to the development of analogous approaches to obtain the q.c.c. values for other quadrupolar nuclei. As soon as a larger collection of data becomes available, this parameter could provide a unique tool for shedding more light on the different values of the field gradient for the same nucleus in different molecules or in different environments in the same molecule.

Experimental

Details of the syntheses of the compounds reported here are in the literature: (1),[6] (2),[11] (3),[12] (4),[13] (5),[14] and (6).[19] Spectra of compounds (1), (4), and (5) were measured at the natural-abundance level of ^{17}O. Compounds (2), (3), and (6) were enriched in ^{17}O to *ca.* 10%. Enrichment was accomplished on the parent precursor carbonyl: $[Fe_2(CO)_9]$ for (2) and $[Os_3(CO)_{12}]$ for (3) and (6), by addition of ^{17}O-enriched carbon monoxide (Prochem., 20%) to hydrocarbon solutions of $[Fe_2(CO)_9]$ and $[Os_3(CO)_{12}]$ each in a sealed vial. The vials were left standing for 4 d, at 318 K for Fe and 388 K for Os.

The ^{13}C (100.6 MHz) and ^{17}O (54.3 MHz) spectra were measured in $CDCl_3$ solution in tubes (outside diameter 10 mm) with a Bruker WH-400 instrument. Spin–lattice relaxation times (T_1) were measured by the standard inversion–recovery technique, and ^{13}C-{^1H} n.O.e.s were obtained by comparison of peak integrations from ^{13}C spectra measured with full ^1H broad-band decoupling and with inverse-gated ^1H broad-band decoupling. Suitable pulse repetition times ($\geqslant 5\ T_1$) were employed for spectral accumulation. The temperature of the samples was actively controlled at 310 K to avoid complications from comparison of results from experiments employing full ^1H broad-band decoupling (*e.g.* ^{13}C T_1 runs) with those without such decoupling (*e.g.* ^{17}O T_1 runs and ^{13}C-{^1H} gated decoupling).

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* If spin rotation were an important mechanism for ^{17}O as it may be for ^{13}C these motions would need to be considered.

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