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¹⁷O NMR SPECTROSCOPY OF TRANSITION METAL CARBONYLS *

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Summary

NMR spectra of ¹⁷O in natural abundance have been obtained for a range of metal carbonyls. Linewidths of less than 10 Hz for the derivatives of Cr, Mo, W and Fe have been observed, although they are slightly larger for the derivatives of metals having an electric quadrupole moment. Comparison with the corresponding ¹³C NMR data shows that: (i) the chemical shift ranges are comparable, (ii) the ordering of chemical shifts is not very different, (iii) the linewidths are more favourable for ¹⁷O than for ¹³C for some Mn and Co derivatives and allow an extension of the range of temperature in which information on the fluxional dynamics are obtainable in the rapid exchange limit.

Introduction

The study of metal carbonyls and their derivatives has been revolutionised by the introduction of ¹³C NMR spectroscopy at natural abundance and has provided a large number of results important to the determination of their chemical bonding, structure [1] and fluxional dynamics [2]. In principle the study of ¹⁷O NMR could have the same impact on the solution of the above problems. There are, however, two major problems for ¹⁷O studies in practice. Firstly, the low sensitivity at natural abundance is unfavourable because the abundance is low (0.037%) and so is the magnetogyric ratio (5.769 MHz T⁻¹), even compared with the case of ¹³C (0.11%; 10.705 MHz T⁻¹). Secondly, since the ¹⁷O nucleus possesses a sizeable electric quadrupole moment ($Q = -2.6 \times$

* Dedicated to Professor Eugene G. Rochow on the occasion of his 70th birthday.

TABLE 1

THE RATIO OF SHIFT RANGE TO AVERAGE LINEWIDTHS FOR ^{17}O AND OTHER NUCLEI ^a

Nucleus	Shift range (R) ^b	Line width (Γ) ^b	Ratio (R/ Γ)
^1H	10^3	1	10^3
^{13}C	10^4	1	10^4
^{17}O	10^4	10^2 – 10^3	10^2

^a Typical values in diamagnetic compounds at 2.3. Tesla. ^b In Hz.

10^{-2} cm^2) very broad resonances (10^2 or 10^3 Hz) are frequently obtained because of rapid nuclear relaxation. This fact not only aggravates the detection problem on high resolution spectrometers but also reduces the effective resolving power of the technique compared, for example, to the situation for carbon where linewidths of the order of 1 Hz, at least in organic molecules, are common. The important parameter here is the ratio of the effective shift range, R , to the linewidth, Γ (both in Hz). for ^{17}O , R/Γ from published data for all types of compound is about 120 or less (shift range of about 12×10^4 Hz and a linewidth of say 10^2 Hz) whereas for ^{13}C the figure is 18×10^4 (range of 18×10^4 Hz linewidth say 1 Hz), see Table 1. Hence ^{17}O studies would appear to offer less than ^{13}C studies in general. Nevertheless, for particular investigations and for some restricted ranges of compounds the technique has already proved useful despite its low resolution.

We report here a survey of ^{17}O results for a range of transition metal carbonyls taken with the objective of determining the utility of the method in high resolution studies. Few papers on the ^{17}O NMR spectroscopy of transition metal organometallic compounds have appeared [3–5]. Additionally for inorganic samples most ^{17}O NMR applications have been for solutes in aqueous solution [3] when viscosity effects are expected to increase the quadrupole induced linewidths.

Results and discussion

The ^{17}O chemical shifts observed for the carbonyl groups at room temperature are reported in Table 2. They are in the range 187–213 ppm upfield from acetone. This is comparable with the corresponding ^{13}C chemical shift range reported in the literature (235–194 ppm downfield from TMS). Additionally the ordering of the ^{17}O shifts is close to that observed for the ^{13}C shifts, although there are some exceptions [5].

The observed linewidths for I, III, IV and VI were limited by the experimental conditions used. In each case they are, however, less than 30 Hz. Values of this order (~ 25 Hz) have been reported recently for some arene chromium(0) tricarbonyls [5]. The linewidths for II, VII, IX and X were measured under higher resolution conditions which revealed much lower values: less than 10 Hz. The value of 2 Hz for II is indeed the smallest value so far reported for a carbonyl group and is not very different from the operational linewidths common in ^{13}C studies. Thus the prospect of high resolution studies in metal carbonyls

by ^{17}O NMR of the same level of utility as ^{13}C NMR studies is good.

In organic molecules the ^{17}O linewidth of CO resonances ranges from several tens to several hundreds of Hz [3]. Thus the bonding of CO's with transition metals, at least for the terminal groups reported here, evidently gives lower electric field gradients at oxygen than in most other cases. The linearity of the M—C—O grouping may be an important factor. The situation is reminiscent of the unusually narrow ^{14}N linewidths found for organic isonitriles, $\text{R}-\text{N}^+\equiv\text{C}^-$.

For V, VI and XI (Γ ^{17}O is up to 50 Hz) broadening may have a component ascribable to the combined effect of J coupling between ^{17}O and each of the metals, and the rapid nuclear relaxation of the latter because of their own electric quadrupole effects (^{55}Mn , $I = \frac{5}{2}$; ^{59}Co , $I = \frac{7}{2}$). ^{13}C studies have been severely hindered because of the same effect [6]: broad signals are generally observed for carbon atoms bound to quadrupolar metals. The result is poor resolution of the stereochemical environment which makes the interpretation of the ^{13}C NMR spectra difficult. Additionally, ambiguity often arises in the case of variable temperature studies in fluxional molecules, since the broadening sometimes observed upon increasing the temperature of the sample could be primarily due to progressively inefficient quadrupole induced relaxation of the metal rather to some exchange process [6]. Inspection of Table 2 shows that the broadening is in fact greater for ^{13}C than for ^{17}O in the same molecule (see results for V, VI, XI). In each case the broadening depends upon the electric field gradient at the metal, its quadrupole moment, the correlation time and the J coupling between the metal and the second nucleus (^{17}O or ^{13}C). The only variable for any one molecule therefore is J , and it follows that 1J -($^{59}\text{Co}-^{13}\text{C}$) $>$ 2J ($^{59}\text{Co}-^{17}\text{O}$) in (X), and 1J ($^{55}\text{Mn}-^{13}\text{C}$) $>$ 2J ($^{55}\text{Mn}-^{17}\text{O}$) in V and VI.

The narrower linewidth for ^{17}O is particularly useful for the study of the stereochemical rigidity of $\text{Mn}_2(\text{CO})_{10}$. ^{13}C NMR spectra of V have shown two broad peaks at room temperature [7]. The observation in the ^{17}O spectrum of two reasonably sharp lines, which moreover stay unchanged up to 130°C , rules out the occurrence of intramolecular carbonyl exchange. These observations will be extended in the future to the study of other samples in which the presence of a metal with $I > \frac{1}{2}$ prevents the attainment of ^{13}C spectra at low temperatures of about -20°C or so.

Some disadvantages in the study of fluxional processes by ^{17}O NMR spectroscopy are on the other hand foreseeable on the basis of the observation of the severe line broadening measured for XI on lowering the temperature. The linewidth of 50 Hz at room temperature becomes 160 Hz at -20°C and 310 Hz at -50°C . Since one resonance only is observed down to -90°C from ^{13}C data [14], the broadening observed is attributed to the quadrupole effect. The linewidth of 240 Hz for XII is ascribed to the superposition of the signal of the CO's bound to the metal with the signal of the carboxyl groups rather than to an incipient freezing of the CO's exchange. In the case of VIII the observation of three signals at room temperature which broaden at $+50^\circ\text{C}$, is consistent with the findings obtained from ^{13}C spectroscopy [8], that carbonyl site exchange occurs: if the linewidth were controlled by the quadrupolar effect the lines should have sharpened at higher temperature. Finally two resonances have been observed for a mixture of the *syn*- and *anti*-isomers $\text{Fe}_2(\text{CO})_5(\text{SCH}_3)_2$ (IX

TABLE 2
 ^{17}O AND ^{13}C CHEMICAL SHIFTS AND LINEWIDTHS AT ROOM TEMPERATURE FOR THE CARBONYL GROUPS BOUND TO THE METAL

Compound	δ (^{17}O) ^{a,b}	δ (^{13}C) ^{c,d}	Reference for δ (^{13}C)
I Cr(CO) ₆	-188.8 (<30, CDCl ₃)	212.1	1
II C ₆ H ₅ N(CH ₃) ₂ Cr(CO) ₃	-190.9 (2, CDCl ₃)	235.0	1
III Mo(CO) ₆	-197.9 (<30, CDCl ₃)	202.0	1
IV W(CO) ₆	-207.3 (<30, CDCl ₃)	192.1	1
V Mn ₂ (CO) ₁₀	-178.4 _{eq} (26, C ₆ D ₄ Cl ₂), 196.9 _{ax} (29)	223.1 _{eq} (150), 212.9 _{ax} (170)	7
VI Cp ₂ Mn(CO) ₃	-188.8 (<30, CDCl ₃)	225.1 (32)	6
VII Fe(CO) ₅	-179.7 (7, 20% C ₆ D ₆)	211.9	13
VIII Fe ₂ (CO) ₆ (C ₆ H ₅) ₂ C ₂ CO ₂ (C ₆ H ₅) ₂	-188.9, 198.8, 201.2 (CDCl ₃) ^e	210.0, 206.9, 206.3	8
IX <i>syn</i> -Fe ₂ (CO) ₆ (SCH ₃) ₂	-190.0 (9, CDCl ₃)	212.3	10
X <i>anti</i> -Fe ₂ (CO) ₆ (SCH ₃) ₂	-192.0 (9, CDCl ₃)	210.3	10
XI Co ₂ (CO) ₆ C ₂ (CH ₂ OH) ₂	-213.6 (50, CH ₃ OD)	200.9 (75)	this work
XII Co ₂ (CO) ₆ C ₂ (CO ₂ CH ₃) ₂	-202.0 (240, CH ₃ OD)	198.2 (92)	14

^a ppm downfield positive relative to acetone, ^b $\Delta\nu_{1/2}$ (Hz) and solvent in parenthesis, ^c ppm downfield positive relative to TMS, ^d If not otherwise stated $\Delta\nu_{1/2}$ is below 1 Hz, ^e $\Delta\nu_{1/2}$ not given since incipient carbonyl exchange occurs.

and X). The resonances have been assigned on the basis that, when the equilibrium is reached the *anti*-isomer is the most abundant [9]. Again the observation of carbonyl site exchange within each isomer parallels the ^{13}C NMR observations [10].

Experimental

The complexes $\text{M}(\text{Cr}, \text{Mo}, \text{W})(\text{CO})_6$, $\text{Mn}_2(\text{CO})_{10}$, $\text{CpMn}(\text{CO})_3$ and $\text{Fe}(\text{CO})_5$ were purchased from Strem Chemicals Inc. $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2\text{Cr}(\text{CO})_3$ [11], $\text{Fe}_2(\text{CO})_6(\text{C}_6\text{H}_5)_2$, $\text{C}_2\text{COC}_2(\text{C}_6\text{H}_5)_2$ [8], *syn*- and *anti*- $\text{Fe}_2(\text{CO})_6(\text{SCH}_3)_2$ [9], $\text{Co}_2(\text{CO})_6\text{C}_2(\text{CH}_2\text{OH})_2$ [12] and $\text{Co}_2(\text{CO})_6\text{C}_2(\text{CO}_2\text{CH}_3)_2$ [12] were prepared by published methods. Deuteriated solvents were purchased from C.E.A. and were used directly after having been dried over molecular sieves. ^{17}O NMR spectra were recorded on a Jeol FX-90Q instrument and on a Bruker WP-200 operating at 12.20 and 27.13 MHz respectively in the Fourier transform mode.

Accumulation times are lowered because of reasonably short T_1 values for ^{17}O compared with ^{13}C which allows rapid pulsing without saturation. A signal to noise ratio of about 13/1 was obtained for the ^{17}O signal of $\text{Cr}(\text{CO})_6$ (0.35 M in CDCl_3 ; 10 mm tube) from 12500 transients each accumulated for 0.2 s and taken with a pulse angle of 45° (5 Hz digital resolution; 10 Hz line broadening parameter introduced) using the WP-200. In each case the ^2D resonance of the solvent was used as the lock signal, and the shift results were adjusted for the different effective fields. The reference signal used was the ^{17}O signal of per-deuteriated acetone either as an internal reference or calculated from the frequency of the lock signal. ^{13}C NMR spectra have been obtained on a Jeol PFT-100 operating at 25.15 MHz in the Fourier transform mode. Solutions were sealed under vacuum in 10 mm tubes.

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