*Journal of Organometallic Chemistry*, 174 (1979) C70--C76
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary Communication

---

# OXYGEN-18 ISOTOPE SHIFTS ON THE $^{13}$C NUCLEAR MAGNETIC RESONANCE OF METAL CARBONYL DERIVATIVES

DONALD J. DARENSBOURG
Department of Chemistry, Tulane University,
New Orleans, Louisiana 70118 (U.S.A.)
(Received May 22nd, 1979)

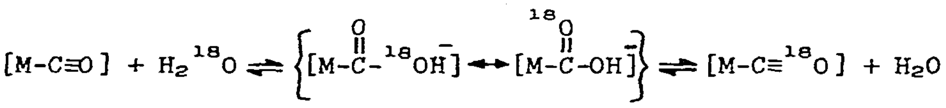
## Summary

The oxygen-18 isotope shifts on the natural abundance $^{13}$C NMR spectra of oxygen-18 enriched samples of $W(CO)_6$ and $W(CO)_5PPh_3$ have been observed to be 0.040 ppm (0.61 Hz at 15.03 MHz) upfield from that of a $^{13}$C nucleus bearing an oxygen-16 atom.

---

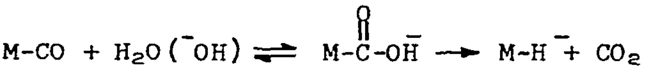
The consequence of isotopic substitution on the magnetic shielding of nuclei has been treated theoretically and subsequently demonstrated to be useful in the monitoring of a variety of chemical processes. In particular, Jameson has concluded that the dominant term contributing to the isotope shift is the anharmonic vibration term with the change in NMR chemical shielding with respect to internal displacement coordinate being negative (the heavier isotopic molecule appears upfield), and that the magnitude of the isotope shift will be proportional to the number of isotopically substituted atoms.[1] Several reports have indicated the utility of this change in chemical shielding upon isotopic substitution in investigations of $^{18}$O-isotope shifts on the $^{31}$P nuclear magnetic resonance of phosphates.[2-5]

Recently the ${}^{18}O$-isotope shift in the ${}^{13}C$ NMR spectrum of <u>tert</u>-butyl alcohol has been observed by Risley and Van Etten, with an upfield shift of 0.035 ppm (0.7 Hz at 20 MHz) being noted.[6] In this communication the oxygen-18 isotope shift on the ${}^{13}C$ NMR spectra of the carbon monoxide ligands in group 6b metal carbonyl derivatives are presented and the general usefulness of this technique in assessing the extent of oxygen-18 incorporation into metal carbonyl species by means of reaction (1) are discussed.



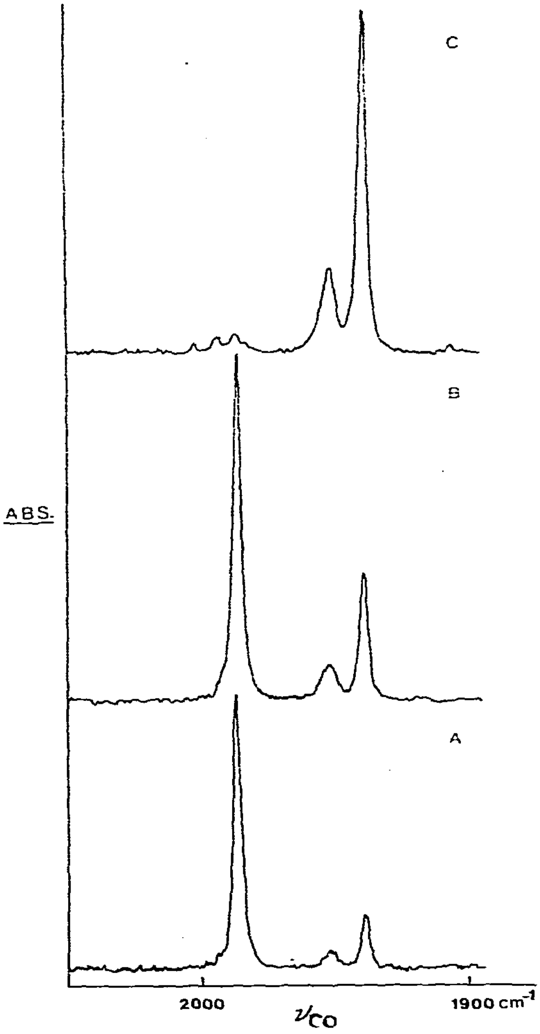
$$[\mathrm{M{-}C{\equiv}O}] + \mathrm{H_2{}^{18}O} \rightleftharpoons \left\{[\mathrm{M{-}\overset{O}{\overset{\|}{C}}{-}{}^{18}O\overline{H}}] \leftrightarrow [\mathrm{M{-}\overset{{}^{18}O}{\overset{\|}{C}}{-}OH}]^{-}\right\} \rightleftharpoons [\mathrm{M{-}C{\equiv}{}^{18}O}] + \mathrm{H_2O} \qquad (1)$$

Oxygen exchange reactions of a variety of cationic and neutral metal carbonyl derivatives with oxygen-18 labelled water have been examined in our laboratory and are believed to proceed <u>via</u> a hydroxycarbonyl intermediate, [MCOOH].[7-11] Concomitantly with the oxygen exchange reaction the hydroxycarbonyl intermediate was also observed to undergo $CO_2$ elimination with metal-hydride formation (eq 2), a process common to the energy-important metal catalyzed water-gas shift reaction.[12-17] Although the neutral metal carbonyl derivatives were shown to be inert to



$$\mathrm{M{-}CO} + \mathrm{H_2O}({}^{-}\mathrm{OH}) \rightleftharpoons \mathrm{M{-}\overset{O}{\overset{\|}{C}}{-}O\overline{H}} \longrightarrow \mathrm{M{-}H^{-}} + \mathrm{CO_2} \qquad (2)$$

oxygen exchange reaction with water (conditions where the cationic metal species readily exchange oxygen atoms), more basic conditions readily promoted the oxygen exchange process. Nevertheless, in basic solutions the rate of metal hydride production has been shown to be enhanced over that of oxygen exchange due to deprotonation of the hydroxycarbonyl intermediate,[11,18] therefore it was necessary to carefully control the basicity of the reaction solution.[19] This was accomplished employing a biphasic reaction system with the organic phase consisting of the neutral carbonyl



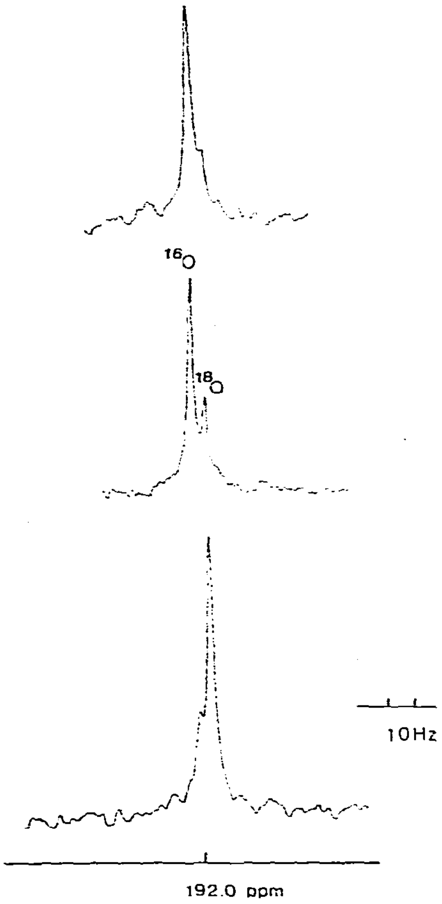


Figure 1. Infrared spectra in the $\nu$(CO) region of mixtures of $W(C^{16}O)_6$ and its highly oxygen-18 enriched analog. Measured oxygen-18 content: A. 17%, B. 28%, and C. 86%.

Figure 2. Natural abundance $^{13}C$ NMR spectra of $W(CO)_6$ observed on mixtures of $W(C^{16}O)_6$ and its highly oxygen-18 enriched analog. Measured oxygen-18 contents were from top to bottom: 15, 25, and 82%

derivative in benzene and an aqueous phase consisting of sodium or potassium hydroxide with a small quantity of tetra-n-butylammonium iodide as a phase-transfer catalyst.

An oxygen-18 enriched sample of tungsten hexacarbonyl was prepared in the following manner. $W(CO)_6$ (2.09 mmol), n-$Bu_4NI$ (0.107 mmol), and 1.0 ml of 0.64 M aqueous KOH (99% $H_2{}^{18}O$ obtained from Norsk Hydro, Norway) in 20 ml of benzene were heated with stirring at 72° for 20 hours. The solvent was removed under vacuum and $W(CO)_6$ was recovered by sublimation at 60° in 78% yield. Figure 1c illustrates the infrared spectrum in the $\nu(CO)$ region of the highly oxygen-18 enriched $W(CO)_6$ sample; whereas Figures 1a-b present spectra of this $^{18}O$-enriched sample diluted with $W(C^{16}O)_6$. The principal $\nu(CO)$ bands in Figure 1 at 1983, 1949, and 1937 $cm^{-1}$ are assignable to an antisymmetric stretching of trans carbonyl groups where the two carbonyl ligands are both $C^{16}O$, one $C^{16}O$ and one $C^{18}O$, and both $C^{18}O$, respectively. The measured intensity of these $\nu(CO)$ absorptions led to the assessed levels of oxygen-18 content in the samples in Figures 1a-c of 17, 28, and 86%. In addition, mass spectral analysis of the highly $^{18}O$-enriched $W(CO)_6$ sample indicated it to be slightly greater than 80% in oxygen-18 content. Therefore, these well-characterized oxygen-18 enriched species provide excellent examples for establishing the magnitude and direction of oxygen-18 isotope shifts on the $^{13}C$ NMR spectra of metal carbonyl derivatives, as well as the use of this displaced chemical shift in quantitatively determining the extent of oxygen-18 incorporation.

An upfield shift of 0.040 ppm (0.61 Hz at 15.03 MHz) in the natural abundance $^{13}C$ NMR spectrum of the carbon monoxide ligand was observed when $^{18}O$ rather than $^{16}O$ is bonded to the carbon in $W(CO)_6$ (Figure 2). The natural abundance $^{13}C$ NMR spectra were recorded on a JEOL FX60 operated at 15.03 MHz with an internal deuterium lock. Samples were run in tetrahydrofuran-$d_8$ solvent in 10 mm tubes. The spectra resulted from the accumulation of 2000 transients employing a sweep width of 500 Hz (16 K data block) with an acquisition time of 16.4 sec, a pulse repetition rate of 20 sec, and a flip angle of 90°. The separation of the $^{13}C$ resonance positions was further verified on a higher field instrument with an upfield shift of 2.68 Hz at 67.9 MHz being observed. The $^{13}C$ NMR spectra in Figure 2 were resolved assuming symmetrical peak shapes (Lorentzian) to arrive at oxygen-18 content in the samples of 15, 25, and 82%, respectively which is in good agreement with that determined by infrared and mass spectral analyses.

In an identical manner the $^{13}C$ NMR spectrum of oxygen-18 enriched $W(CO)_5PPh_3$ (sample prepared in a manner similar to that described for $W(C^{18}O)_6$ and purified by recrystallization from $CHCl_3/CH_3OH$ at - 0°) in $CDCl_3$ solvent was observed to exhibit an upfield shift of 0.040 ppm in the $^{13}C$ resonance of the equatorial carbonyl groups at 197.5 ppm ($J_{P-C}$ = 7.3 Hz). Analysis of the peak areas of the $^{13}C^{16}O$ and $^{13}C^{18}O$ $^{13}C$ resonances indicated approximately 30% of the equatorial oxygens were oxygen-18 atoms. On the other hand, the $^{13}C$ resonance of the axial CO group at 199.3 ppm ($J_{P-C}$ = 22.0 Hz) was found to display only a small $^{18}O$-isotope shifted component of -0.040 ppm (< 10% axial oxygen atoms being labelled), thus indicating that during the early stages of oxygen incorporation the exchange is stereoselective. It would nevertheless be anticipated that some of the axial CO groups will bear oxygen-18 atoms even if the oxygen exchange reaction is completely stereospecific since we have observed some scrambling of axial and equatorial CO ligands in <u>cis</u>-$M(CO)_4(^{13}CO)L$ derivatives, including $W(CO)_5PPh_3$, under the conditions of the oxygen exchange process.

These investigations have demonstrated the feasibility of measuring the $^{18}O$-isotope shift upon the natural abundance $^{13}C$ NMR spectra of metal carbonyl derivatives using a FT instrument operating at 15.03 MHz. Clearly this isotope shift provides a useful means for monitoring the rate and site specificity (in stereochemically rigid molecules where more than one type of carbonyl ligand is present) of oxygen exchange processes. Indeed this technique should furnish a quantitative measure of the extent of oxygen-18 incorporation into metal carbonyl clusters as well as in the corresponding hydride derivatives (eq 2), thus providing a means for determining the relative rates of oxygen-incorporation vs metal hydride formation in these systems which are of catalytic importance.

**Acknowledgement.** The financial support of this research by the National Science Foundation through Grant CHE 78-01758 is greatly appreciated.

## References

1. C. J. Jameson, J. Chem. Phys., **66** (1977) 4983.
2. J. Bock and M. Cohn, J. Biol. Chem., **253** (1978) 4082.
3. D. R. Webb, G. G. McDonald, and D. R. Trentham, J. Biol. Chem., **253** (1978) 2908.
4. G. Lowe and B. S. Sproat, J. C. S. Chem. Comm., (1978) 565.
5. R. L. Van Etten and J. M. Risley, Proc. Natl. Acad. Sci. U.S.A., **75** (1978) 4784.
6. J. M. Risley and R. L. Van Etten, J. Am. Chem. Soc., **101** (1979) 252.
7. D. J. Darensbourg and D. Drew, J. Am. Chem. Soc., **98** (1976) 275.

8. D. J. Darensbourg and J. A. Froelich, J. Am. Chem. Soc., **99** (1977) 4726.

9. D. J. Darensbourg and J. A. Froelich, J. Am. Chem. Soc., **99** (1977) 5940.

10. D. J. Darensbourg, Israel J. Chem., **15** (1977) 247.

11. D. J. Darensbourg and J. A. Froelich, J. Am. Chem. Soc., **100** (1978) 338.

12. R. M. Laine, R. G. Rinker, and P. C. Ford, J. Am. Chem. Soc., **99** (1977) 253.

13. H. C. Kang, C. H. Mauldin, T. Cole, W. Slegeir, K. Cann, and R. Pettit, J. Am. Chem. Soc., **99** (1977) 8323.

14. C.-H. Cheng, D. E. Hendriksen, and R. Eisenberg, J. Am. Chem. Soc., **99** (1977) 2791.

15. R. B. King, C. C. Frazier, R. M. Hanes, and A. D. King, Jr., J. Am. Chem. Soc., **100** (1978) 2925.

16. P. C. Ford, R. G. Rinker, C. Ungermann, R. M. Laine, V. Landis, and S. A. Moya, J. Am. Chem. Soc., **100** (1978) 4595.

17. D. J. Darensbourg, M. Y. Darensbourg, R. R. Burch, Jr., J. A. Froelich, and M. J. Incorvia, Adv. Chem. Ser., **173** (1979) 106.

18. D. J. Darensbourg and J. A. Froelich, Inorg. Chem., **17** (1978) 3300.

19. D. J. Darensbourg, M. Y. Darensbourg, N. Walker, J. A. Froelich, and H. L. C. Barros, Inorg. Chem., **18** (1979) 1401.