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High-Field Oxygen-17 Nuclear Magnetic Resonance Spectroscopic Observation of $^{17}O_2$ in Vaska's Compound ($Ir(CO)X(O_2)(PPh_3)_2$; X = Cl, I) and in $Pt(O_2)(PPh_3)_2$

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The structures of the dioxygen adducts of a number of complexes of the Group 8 elements, such as $Ir(CO)Cl(O_2)(PPh_3)_2$ from Vaska's compound (*1*), and of $Pt(O_2)(PPh_3)_2$ (*2*), have been the topic of a number of papers, and the interpretations of both X-ray (*3*), infrared (*4*), and nuclear magnetic resonance studies of these and related systems have been the topic of some debate (*5*). Detailed analysis of such results are of general interest since they may be broadly related to the topic of metal–dioxygen bonding in various industrial, and even biological, systems. In our group, we are particularly interested in the topic of iron–oxygen bonding in proteins, and are attempting to study these interactions by means of ^{57}Fe (*6*) and ^{17}O NMR.

Previous attempts at observing $^{17}O_2$ resonances in proteins have understandably been unsuccessful because of the large ^{17}O linebreadths anticipated due to slow molecular tumbling. More surprisingly, however, attempts at observing the ^{17}O NMR spectra of the O_2 adducts of Vaska's compound, $Ir(CO)Cl(O_2)(PPh_3)_2$, have also been unsuccessful, as have similar investigations of $Pt(O_2)(PPh_3)_2$ (*5*). Early studies by Lapidot and Irving (*7*) on $Ir(CO)X(O_2)(PY_3)_2$ (X = Cl or I, Y = Ph; X = Cl, Y = C_7H_7) by continuous wave NMR at approximately 11 MHz, using 95% ^{17}O-labeled species, did not yield ^{17}O NMR spectra, and it was concluded that the lack of any detectable signal was due to the slow tumbling of the complex, rather than to too few ^{17}O nuclei, dilution of ^{17}O by ^{16}O, the presence of paramagnetic impurities, or rapid exchange between free para- and bound diamagnetic oxygen (*7*). Later attempts by Lumpkin *et al.* (*8*) at 8.1 MHz also failed to detect an NMR signal, although these workers did determine the ^{17}O quadrupole coupling constants and asymmetry parameters for the solid Cl and Br adducts (O_1: e^2qQ/h = 16.9 MHz, η = 0.65; O_2: e^2qQ/h = 15.6 MHz, η = 0.91). These results imply peroxidic oxygen (O_2^{2-}) for both the Cl and Br species (*8*).

More recently, Postel *et al.* (*5*) have observed the ^{17}O NMR spectra of a number of oxoperoxometal (W, Mo, V) complexes, but have been unable to observe any signal for $M(O_2)(PPh_3)_2$ (M = Pt or Pd, 10% $^{17}O_2$), even when recording spectra on a 400 MHz (^1H) NMR spectrometer. They conclude that in the case of complexes of the Group 8 metals which reversibly bind dioxygen, it is most likely exchange with paramagnetic molecular dioxygen that causes line broadening, to such an extent that the

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$M(^{17}O_2)$ line becomes undetectable, a conclusion opposite to that of Lapidot and Irving (*7*). Finally, Curci *et al.* have observed ^{17}O resonances from chromium and molybdenum oxide diperoxides (*9*), but once again assert that serious difficulties are to be expected with ^{17}O NMR of transition metal–dioxygen complexes, due to exchange with paramagnetic dioxygen and/or slow molecular tumbling (*5*).

To try to resolve the precise reasons for the difficulties in observing such signals, which have relevance to any future studies of proteins, we have repeated the experiments of these previous workers using highly labeled $^{17}O_2$ (40% $^{17}O_2$), together with a "home-built" high-field (11.7 T) spectrometer, and we now report the rapid observation of ^{17}O NMR signals from both IrO_2 and PtO_2 systems.

We show in Fig. 1 the ^{17}O NMR spectra (taken at 67.8 MHz, corresponding to a magnetic field strength of 11.7 T) of $Ir(CO)Cl(^{16}O_2)(PPh_3)_2$, $Ir(CO)Cl(^{17}O_2)(PPh_3)_2$ and their difference spectrum (Fig. 1A), of $Ir(CO)I(^{16}O_2)(PPh_3)_2$, $Ir(CO)I(^{17}O_2)(PPh_3)_2$ and their difference spectrum (Fig. 1B), and of $Pt(^{16}O_2)(PPh_3)_2$, $Pt(^{17}O_2)(PPh_3)_2$ and their difference spectrum (Fig. 1C). The results of Fig. 1 illustrate the following points: (1) ^{17}O NMR spectra of some Group 8 metal–oxygen complexes, including the oxygen adducts of Vaska's Cl and I compound, and of $Pt(O_2)(PPh_3)_2$, can be obtained. (2) The chemical shifts of Vaska's Cl and I dioxygen adducts, $(Ir(CO)X(O_2)(PPh_3)_2)$ are very similar, 325 ppm for X = Cl and 350 ppm for X = I. This implies an essentially equivalent bonding in the IrO_2 fragment in both the reversible (Cl) and irreversible (I) species. (3) The chemical shifts observed for all MO_2 fragments (325–385 ppm) are quite close to the value of about 269–281 ppm found for di-*t*-butylperoxide, (*9, 10*)

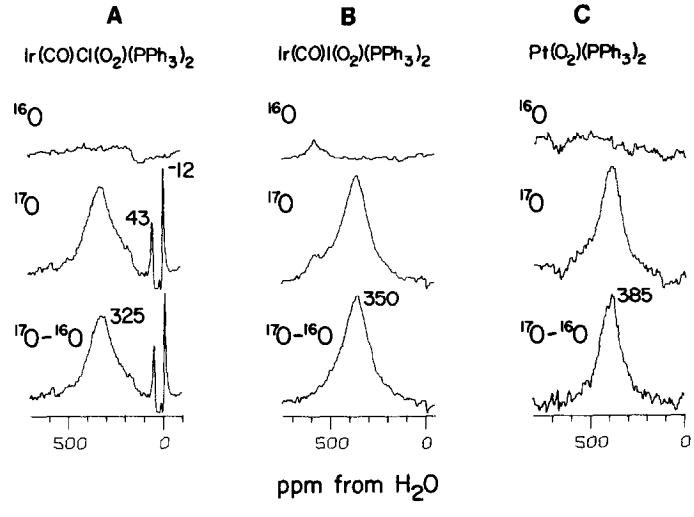

FIG. 1. Oxygen-17 NMR spectra of O_2 adducts of Vaska's Cl and I compound, and of $Pt(O_2)(PPh_3)_2$, in $CHCl_3$. Spectra were obtained using an 11.7 T Fourier transform NMR spectrometer (corresponding to an ^{17}O resonance frequency of 67.8 MHz). (A) $Ir(CO)Cl(O_2)(PPh_3)_2$ containing $^{16}O_2$ or $^{17}O_2$, and their difference spectrum. (B) As (A) but for the I complex. (C) $Pt(O_2)(PPh_3)_2$ containing $^{16}O_2$, $^{17}O_2$, and their difference spectrum. Impurity peaks (sharp lines) are observed in (A) and have also been observed in (C) after leaving the sample for some hours at room temperature, and are tentatively attributed to triphenylphosphine oxide (43 ppm), ethanol (7 ppm), and phosgene (−12 ppm).

strongly suggesting *peroxidic* oxygen in all three complexes. (4) The linewidths of both the Cl and I Vaska dioxygen complex are essentially identical (~10 kHz), ruling out significant chemical exchange broadening, and are very similar to that observed in the (irreversible) Pt complex (~9 kHz). Since the linewidths observed are all very broad, then previous unsuccessful attempts at observing them can be attributed primarily to their great width. In particular, use of long acquisition delays to eliminate "pulse breakthrough" also eliminates most signal since the spin–spin relaxation time of ^{17}O in these complexes is only ~30 μs. (5) Only one ^{17}O NMR signal is observed in the Vaska complexes, in contrast to the resolution of two NQR signals, but this may presumably be attributed to some type of "crystal-packing" effect in the NQR study.

The results we have obtained above, which are all consistent with ^{13}C and ^{31}P NMR studies on the same materials (data not shown), thus indicate that the ^{17}O NMR spectra of a variety of Group 8 MO_2 complexes may be recorded, but because of the great linewidths involved, special consideration needs to be paid to data acquisition conditions so that only a minimal amount of signal is lost prior to data accumulation. In addition, as might be expected, special consideration needs to be given to sample temperature and solvent viscosity in order for signals to be observed. For example, for Vaska's Cl compound in $CHCl_3$, we obtain a good spectrum at 45°, LW = 8800 Hz, η/T = 0.014 mP K^{-1}, while at −6°, considerable signal intensity is lost due to more rapid relaxation since η/T = 0.028, corresponding to a T_2 of ~17 μs. Using the reported e^2qQ/h and η values (*8*), we obtain a rotational correlation time (τ_R) of 100 ± 10 ps for both the Cl and I species at 20°. The same correlation times are also obtained from ^{13}C spin–lattice (T_1) relaxation-time measurements of C^δ (T_1 ~ 0.57 s, τ_R = 95 ± 10 ps and 100 ± 10 ps for the Cl and I species, respectively). Based on the similar molecular size, shape, and linewidths for the Ir and Pt complexes, our results imply e^2qQ/h ~ 16 MHz for $Pt(^{17}O_2)(PPh_3)_2$ also.

We thus conclude that ^{17}O NMR studies of the Group 8 metal–dioxygen adducts are, in fact, quite feasible. In suitable cases, spectra may be obtained with only a few minutes of data acquisition, since $T_1 = T_2$ ~ 30 μs, and extremely rapid recycle times may be used, so sample decomposition effects can be minimized. For the O_2 adducts of Vaska's Cl and I compound (containing IrO_2 units) and in $Pt(O_2)(PPh_3)_2$, our results imply exclusively peroxidic oxygen, with large e^2qQ/h values, rather than O_2 exchange, as being the primary contributor to the observed broad (~10 kHz) ^{17}O NMR linewidths.

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