Oxygen-17 Nuclear Magnetic Resonance Spectroscopy and Iridium and Rhodium Molecular Oxygen Complexes

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The $^{17}O_2$ complexes of $IrCOX(PY_3)_2$ (X = Cl or I, Y = Ph; X = Cl, Y = C_7H_7) were prepared and their continuous-wave ^{17}O n.m.r. spectra were recorded for chloroform solutions. No resonance attributable to bound $^{17}O_2$ could be detected 20,000 p.p.m. up- and down-field from resonance of $H_2{}^{17}O$. Failure to observe the $^{17}O_2$ resonance could not be attributed to (i) few nuclei, (ii) dilution of bound $^{17}O_2$ by $^{16}O_2$, (iii) the presence of paramagnetic impurities, or (iv) rapid exchange between free para- and bound dia-magnetic oxygen. Similarly, the ^{17}O resonance of $IrCOI[P(C_7H_7)_3]_2S^{17}O_4$ could not be detected, which suggests that Vaska type complexes tumble at a rate which broadens the resonances beyond detection.

As the number of metal complexes containing co-ordinated oxygen increases,[1] its chemistry and electronic structure are of increasing interest. Although ligated oxygen has been subjected to a variety of spectroscopic [2] and crystallographic [3] studies, a fundamental question concerning its electronic structure remains unanswered. In the case of the Vaska type complexes [(Ia), (Ib), and (II)] whose structures have been determined by *X*-ray crystallography, the bond length of co-ordinated oxygen can be interpreted as representing either superoxide (or peroxide) ion or an electronically excited state of molecular oxygen.[4]

The Vaska compounds are diamagnetic [5] and can be prepared with $^{17}O_2$ in the place of $^{16}O_2$, making them apparently ideal candidates for the application of ^{17}O n.m.r. spectroscopy to the characterization of the ligated oxygen. Such chemical shifts have proved to be sensitive indicators of the bond character of the $C-{}^{17}O$ bond.[6] It was hoped that the bond character of ligated oxygen might similarly be revealed by its ^{17}O chemical shift. We have searched for the ^{17}O-resonances of $^{17}O_2$ ligated to (I) and (II) and here report a series of experiments, which point out the limitations of ^{17}O measurements of this kind.

$IrCOX(PY_3)_2$

	X	Y
(Ia)	Cl	Ph
(Ib)	I	Ph
(Ic)	Cl	C_7H_7
(Id)	I	C_7H_7

$[Re(diphos)_2]Cl$
(II)
diphos = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$

EXPERIMENTAL

Reagents.—Labelled water (^{17}O, 10%) and oxygen (^{17}O, 95%) were obtained from the Isotope Separation Plant of the Weizmann Institute. Chloroform (Fluka Spectrograde) was passed through an alumina column before use, unless otherwise noted. Labelled sulphur dioxide was prepared by burning sulphur in a vessel which had been evacuated and then filled (700 mmHg) with $^{17}O_2$ (^{17}O, 50%). Upon completion of combustion, sulphur dioxide was frozen into a side-arm at liquid nitrogen temperature and unreacted molecular oxygen was recovered. The side-arm was then heated to room temperature and the sulphur dioxide transferred to a storage vessel. The isotopic composition of the sulphur dioxide was determined by mass spectrometric analysis based on the 48—50 *m/e* peaks and was shown to be identical to that of reactant molecular oxygen. The sulphur dioxide was used without further purification.

Preparation of Compounds for N.m.r. Study.—*Chlorocarbonylbis(triphenylphosphine)iridium*(I) (Ia). This was commercial grade (Strem Chemicals) and was used without further purification.

Chlorocarbonylbis(tritolylphosphine)iridium(I) (Ic). This was prepared by the method of ref. 3(*b*).

Iodocarbonylbis(triphenylphosphine)iridium(I) (Ib) and *Iodocarbonylbis(tritolylphosphine)iridium*(I) (Id). These were prepared from (Ia) and (Ic), respectively, by the method of ref. 3(*b*).

Bis[bis(diphenylphosphino)ethane]rhodium(I) *chloride* (II). This was prepared by the method of ref. 7.

Iodosulphatocarbonylbis(tritolylphosphine)iridium(I) (III). This was prepared from the $^{17}O_2$ complex of (Id) (see later) and $S^{17}O_2$ (^{17}O, 50%) by the method of ref. 8. $\nu_{max.}$ (KBr): 1287vs, 1284vs, 1154vs, 1144vs, 878m, 877m, 864m, 861m, 846m, 840m, 654m, 647m, 616w, 605w, 541m cm^{-1}, which correspond to the vibrations of labelled co-ordinated sulphate containing 75% ^{17}O.

^{17}O-*Triphenylphosphine oxide.* This was prepared by a variation of the method of ref. 9 by hydrolysing triphenylphosphine dibromide in dioxans and $H_2{}^{17}O$ (^{17}O, 10%; 9 : 1). It was recrystallized from hot methanol; its oxygen-17 content was 2·5%.

^{17}O-1,2-*Bis(diphenylphosphinyl)ethane.* This was separated (by liquid chromatography on a silica-gel column, using an increasing benzene–chloroform gradient as the eluting solvent) from a mixture of (II) (300 mg), bis(diphenylphosphino)ethane (100 mg), and oxygen-17 (10 ml

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s.t.p.; ^{17}O 95%) which had been shaken for 5 days. The fraction of ^{17}O-1,2-bis(diphenylphosphinyl)ethane was characterized by comparison of its i.r. spectrum with that previously reported.[10]

Preparation of Oxygen-17 *Complexes*.—Chloroform solutions (2 ml) of (Ia) (30 mg, 0·038 mol), (Ib) (30 mg, 0·034 mol), (Ic) (300 mg, 0·36 mol), (Id) (300 mg, 0·33 mol), and (II) (300 mg, 0·32 mol), in a 15 mm (o.d.) tube with a breakable seal, were vigorously degassed. Oxygen-17 (^{17}O, 95%; 5 ml s.t.p.) was admitted to the tube by use of a Toepler pump; the tube was cooled to liquid nitrogen temperature and sealed. The resulting pressure of oxygen above the sample was *ca.* 3 atmospheres.

Recovery of Oxygen Gas and Complexes.—Upon completion of the n.m.r. measurements, the sample was frozen to liquid-nitrogen temperature and the break-seal broken; the oxygen gas was recovered and its isotopic content determined by mass spectrometric analysis of the 32—36 *m*/*e* peaks. The ^{17}O content of the recovered oxygen was 95%. In the case of (Ib) and (Id) methanol was added to the chloroform solution; a precipitate was obtained, whose i.r. spectrum was identical to that of the oxygen complex of (Ib) and (Id) and had $\nu_{max.}$ (KBr) at 863w and 838vs cm^{-1} ($^{16}O-^{16}O$ and $^{17}O-^{17}O$ stretching, respectively).

Physical Measurements.—The ^{17}O n.m.r. spectra were recorded in the V mode on a Varian DA 60 spectrometer using a 20 Hz audio frequency modulation and a V 4210 variable-frequency unit operating at 8·00 KHz. Combinations of modulation amplitudes and radio-frequency powers varying from 0·5 to 5 and 0·1 to 1 G, respectively, were used in scans 20,000 p.p.m. up- and down-field from the $H_2{}^{17}O$ signal at $\sigma = 0$.

Mass spectrometric analysis were performed on a C.E.C 21 401 spectrometer. E.s.r. measurements were made on a Varian E 12 spectrometer. I.r. measurements were made on a Perkin-Elmer 125 spectrometer. ^1H N.m.r. spectra were obtained on a Bruker XL 100 spectrometer.

RESULTS AND DISCUSSION

The ^{17}O n.m.r. spectra of chloroform solutions of the $^{17}O_2$ complexes of compounds (Ia—d) and (II) a few hours after oxygenation displayed no resonances 20,000 p.p.m. up- and down-field from the $H_2{}^{17}O$ signal at $\sigma = 0$. Several days later a resonance was observed at −5 p.p.m. However, when solutions were prepared with chloroform which had been passed through an alumina column, the resonance was not observed. Furthermore, when methanol was added to the purified chloroform, the solutions displayed a resonance at +37 p.p.m. Since the ^{17}O chemical shifts of methanol and ethanol are +37 and −5 p.p.m., respectively, we assign the peaks observed to ^{17}O-labelled alcohol, which must have been formed by a catalysed oxygen exchange between alcohol and $^{17}O_2$.

During the course of our study, we observed that solutions of (Ia—d) a day after oxygenation gave a faint resonance at −46 p.p.m. which grew in intensity during several days. The peak appeared sooner and grew faster upon addition of a 5 mol excess of triphenylphosphine to solution of (Ia). An authentic sample of $^{17}OPPh_3$ (2·5%) was prepared and its ^{17}O resonance also appeared at −46 p.p.m. On the basis of these data and the fact that (Ia) and (Ib) are known to decompose to triphenylphosphine oxide,[10] we assign the resonances, which we observed for solutions of (Ia—d) to the corresponding phosphine oxides. Similarly, a solution of (II) displayed a resonance at −56 p.p.m. When a solution was prepared containing an 8 mol excess of bis(diphenylphosphino)ethane the resonance was more intense. After a week, ^{17}O-1,2-bis(diphenylphosphinyl) ethane was isolated from this solution, and was found to have a ^{17}O chemical shift of −56 p.p.m. To recapitulate, we were unable to observe any resonances belonging to $^{17}O_2$ bound to (I) or (II).

Our failure to observe the ^{17}O resonance of co-ordinated $^{17}O_2$ cannot be attributed to an insufficient number of ^{17}O nuclei in the sample, assuming the bandwidth of the resonance is similar to that of other ^{17}O labelled compounds. Our limit of detection was 2×10^{-7} g atom cm^{-3} for $H_2{}^{17}O$ whereas the amounts of oxygen-17 bound to (Ia—d) and (II) were 7·7, 6·8, 73·0, 65·6, and 64·4 $\times 10^{-5}$ g atom cm^{-3}, respectively. To check whether $^{17}O_2$ was diluted by $^{16}O_2$ during the course of sample preparation, upon completion of our measurements, the oxygen gas was recovered and mass spectrometric analysis showed that the initial isotopic composition had not changed. To verify that $^{17}O_2$ was bound to (Ib) and (Id), which irreversibly bind oxygen and might have bound $^{16}O_2$ before degassing was completed, the complexes were recovered and the amount of co-ordinated $^{17}O_2$ was determined by i.r. analysis of the oxygen-stretching frequency. The ratio of the $^{17}O-^{17}O$ band to the $^{16}O-^{16}O$ band showed that no dilution of co-ordinated oxygen had taken place.

Our assumption that the band-width of co-ordinated $^{17}O_2$ is similar to that for covalently bound oxygen in small molecules must be reconsidered. A rapid exchange between free paramagnetic $^{17}O_2$ and co-ordinated $^{17}O_2$ would broaden the resonance signal. Although such a rapid exchange might occur in (Ia) and (Ic), which bind oxygen reversibly, it certainly cannot be occurring in (Ib) and (Id), which bind oxygen irreversibly. Resonances are often broadened by the presence of paramagnetic species. To exclude this possibility we recorded the e.s.r. spectra of solutions of (Ia), (Ib), and (II) and detected no significant resonance signals. Furthermore, the proton magnetic resonance signals of the phenyl group of (II) and the tolyl methyl group of (Ic) were not significantly broadened upon oxygenation of the complexes, additional evidence against the paramagnetism of the solutions.

Our inability to observe the resonances of these diamagnetic complexes must stem from some physical property of the complex itself. The linewidth of a nucleus which possesses a nuclear spin quantum number >1/2, such as oxygen-17, is determined by the interaction of the electric nuclear quadrupole moment of the

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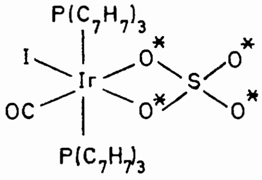
nucleus and the electric field gradient. This interaction, which results in broad band-widths, is attenuated by fast tumbling of the molecule, equation (1), where $(^1T_2)_Q$ is the linewidth, I is the nuclear spin quantum number, eQ is the electric nuclear quadrupole moment of the oxygen-17 nuclei, eq is the electric field gradient, and τr is the rotational correlation time of the complex.[11]

$$(^1/T_2)_Q = \frac{3}{40}\cdot\frac{2I+3}{I^2(2I-1)}\left[\frac{e^2Qq}{h}\right]^2\tau r \qquad (1)$$

In the case of our complexes, a very wide line might result from either a very large electric field gradient around the oxygen-17 nuclei, which may be peculiar to co-ordinated molecular oxygen, or a moderately large electric field gradient and a slow tumbling rate, *i.e.* a large τr. To distinguish between these two cases, we have prepared $IrCOI[P(C_7H_7)_3]_2S^{17}O_4$ (III), whose SO_4 ligand is labelled with 75% oxygen-17. No resonances were observed in the ^{17}O n.m.r. spectrum of (III), *i.e.* the resonances of both *endo-* and *exo*-cyclic oxygen-17 nuclei were broadened beyond recognition. Since the resonances of other $S^{17}O_4$ groups are not particularly broad, we can assume that the electric field gradient of a sulphate group is not unusually large. This forces us to conclude that our failure to observe the oxygen-17 resonances of $S^{17}O_4$ and $^{17}O_2$ co-ordinated to the irridium complex (I), stems from the slow tumbling rate of the complex.



(III)

These experiments again emphasize the fact that the continuous-wave ^{17}O n.m.r. technique is of value only in the study of relatively fast-tumbling molecules. If the technique is to be used to probe the nature of co-ordinated oxygen, studies should be done on smaller, faster-tumbling complexes.

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