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Absorption/Desorption of Labelled Dioxygen by the Haem Analogues, $Mn(PR_3)X_2$

MICHAEL BARBER, ROBERT S. BORDOLI, AFSHIN HOSSEINY, KARL MINTEN, CARL R. PERKIN, R. DONALD SEDGWICK and CHARLES A. McAULIFFE

Chemistry Dept., U.M.I.S.T., Manchester M60 1QD, U.K.

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Following our successful isolation of a member of simple coordination complexes $Mn(PR_3)X_2$ (R = alkyl, aryl; $R_3 \neq Ph_3$; X = Cl, Br, I, NCS) which mimic to a remarkable degree the dioxygen transport and storage proteins haemoglobin and myoglobin [1, 2], we now wish to report part of our studies on the detailed manganese dioxygen interaction. It is well known that in cases of chemisorption of dioxygen on metal surfaces 'scrambling' of $^{16}O_2$ and $^{18}O_2$ occurs yielding some ^{16}O–^{18}O on desorption. We have thus carried out a careful mass spectral analysis of mixtures of $^{16}O_2/^{18}O_2$ absorbed and desorbed by a number of our manganese complexes.

Solid complexes $Mn(PPhMe_2)X_2$ (X = Br, I), $Mn(PPhEt_2)Br_2$, $Mn(PPr^n_3)Br_2$ and $Mn(PBu^n_3)I_2$ (see below* for elemental analyses) undergo extremely rapid reaction with dioxygen in the solid state (surface completely dioxygenated < 3 seconds in air) and in solution in a number of solvents (complete dioxygenation in THF may be completed in ⩽8 minutes), both reactions being reversible by means of a pressure-swing (P_{O_2}) drop or by a P_{O_2} drop accompanied by warming:

$$Mn(PR_3)X_2 \underset{-O_2}{\overset{+O_2}{\rightleftharpoons}} Mn(PR_3)X_2{\cdot}O_2$$

In our studies to investigate if the integrity of absorbed dioxygen remains upon desorption we adopted the following procedure: Dioxygen-18 (99%, British Oxygen Company) was mixed in various proportions with ^{16}O–^{16}O by means of a Toepler apparatus and this gas mixture was analysed by mass spectral techniques prior to absorption by the $Mn(PR_3)X_2$ complex, Table I. Once analysed the gas mixture was absorbed onto a solid sample of the complex in a small bulb attached to the Toepler apparatus. After 1 hour the gas was desorbed under vacuum and collected in the Toepler pump. Since the dioxygenated complexes are vividly coloured ($Mn(PR_3)X_2{\cdot}O_2$: purple for X = Cl, blue X = Br, green X = I, red X = NCS), desorption was considered to be complete when the complex decolourised. The desorbed gas was then analysed by mass spectroscopy. In order to examine the mechanism of absorption/desorption over many cycles this procedure was repeated varying numbers of times using labelled O_2 for each complex, Table I. Within experimental error no difference between ^{16}O–$^{16}O/^{18}O$–^{18}O gas composition was observed between the mixture absorbed and desorbed. In particular, no increase in the natural level of gas of molecular weight 34

TABLE I. Summary of Absorption–Desorption Data.

	Before Absorption		After Desorption		Cycle
	$\%^{16}O$–^{16}O	$\%^{18}O$–^{18}O	$\%^{16}O$–^{16}O	$\%^{18}O$–^{18}O	
Solid					
$Mn(PPhMe_2)I_2$	66.7	33.3	66.1	33.9	1
$Mn(PPhEt_2)Br_2$	68.2	31.8	68.3	31.7	3
$Mn(PPr^n_3)Br_2$	61.2	38.8	61.5	38.5	14
$Mn(PPhMe_2)Br_2$	66.2	33.8	65.3	34.7	79
Solution					
$Mn(PBu^n_3)I_2$	47.1	53.0	46.0	54.0	1
$Mn(PPhMe_2)Br_2$	72.8	27.2	74.0	26.0	18
$Mn(PPhEt_2)Br_2$	57.4	42.6	58.2	41.8	26

**Analysis*: Calc. (% Fd.): $Mn(PPhMe_2)Br_2$: C, 27.1 (27.0); H, 3.1 (3.1); Br, 45.3 (45.7); Mn, 15.6 (16.0); P, 8.8 (8.8). $Mn(PPhMe_2)I_2$: C, 21.5 (21.5); H, 2.5 (2.6); I, 56.8 (57.0); Mn, 12.3 (12.6); P, 6.9 (6.8). $Mn(PPhEt_2)Br_2$: C, 31.5 (31.6); H, 3.9 (4.1); Br, 41.9 (42.0); Mn, 14.4 (14.4); P, 8.1 (8.2). $Mn(PPr^n_3)Br_2$: C, 28.8 (29.0); H, 5.6 (5.9); Br, 42.6 (42.7); Mn, 14.6 (14.9); P, 8.3 (8.5). $Mn(PBu^n_3)Br_2$: C, 34.5 (34.5); H, 6.5 (6.8); Br, 38.5 (38.3); Mn, 13.2 (13.3); P, 7.4 (7.6). $Mn(PBu^n_3)I_2$: C, 28.2 (28.4); H, 5.3 (5.5); I, 49.7 (49.9); Mn, 10.8 (11.1); P, 6.1 (6.2).

a.m.u., corresponding to a 'scrambled' $^{16}O-^{18}O$, was observed.

We found similar results for absorption/desorption by tetrahydrofuran solutions of $Mn(PR_3)X_2$, Table I. The dioxygen uptake characteristics of THF solutions of $Mn(PR_3)X_2$ was first examined by electronic spectral changes corresponding to 1:1 Mn complex:O_2 absorption as measured by a gas burette and allowing for absorption by the THF [2, 3][†]. Hence, it was possible to ensure 100% dioxygenation of a given complex. With this information we could employ 10 cm^3 of solution of a given $Mn(PR_3)X_2$ complex and, under identical conditions of pressure and temperature, it was possible to produce 100% absorption of the given $^{16}O-^{16}O/^{18}O-^{18}O$ mixture. Desorption from each $Mn(PR_3)X_2 \cdot O_2$ complex varied according to the isotherm of each complex [3]. For example, although absorption by each complex was at cardice temperature, desorption from $Mn(PBu^n_3)I_2 \cdot O_2$ was achieved merely by applying a vacuum, but from $Mn(PPhMe_2)Br_2 \cdot O_2$ application of a vacuum and warming to 0 °C was necessary to achieve desorption. Before gas collection in the Toepler apparatus the THF solvent was removed by passing through a series of liquid nitrogen traps (only a trace of THF was subsequently detected by mass spectroscopy). As with our solid state experiments absorption/desorption in THF solution of $^{16}O-^{16}O/^{18}O-^{18}O$ mixtures did not involve any oxygen–oxygen bond breaking.

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[†] We warn that attempting to study absorption of dioxygen in acetonitrile solution is pointless. Irreversible oxidation to manganese(III) occurs almost instantaneously [4].