Inorganica Chimica Acta, 45 (1980) L195–L196
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Dibromotri-n-butylphosphinemanganese(II), a Remarkably Close Analogue of Myoglobin

CHARLES A. McAULIFFE and HUSSEIN AL-KHATEEB

Department of Chemistry, University of Manchester, Institute of Science and Technology, Manchester M60 1QD, U.K.

Received June 3, 1980

Upon contact with dioxygen colorless solutions of $Mn(PR_3)X_2$ begin to color as the complex $Mn(PR_3)X_2{\cdot}O_2$ forms [1, 2]. The formation of the latter is a function of the partial pressure of dioxygen and since this can be followed spectrophotometrically it is possible to construct dioxygen-binding curves or 'isotherms' for solution dioxygenation. That these $Mn(PR_3)X_2$ complexes do bind dioxygen in solution is shown in Fig. 1, a plot of dioxygen absorbed (measured by gas burette) against complex concentration. The slope of almost exactly 1 indicates a 1:1 stoichiometry $Mn(PR_3)X_2{\cdot}\ O_2$ in solution and the value of the intercept 7.8×10^{-4} mole dioxygen for 100 cm³ tetrahydrofuran corresponds almost exactly to that obtained for a 100 cm³ THF blank (8.05×10^{-4} mole O_2). In all experiments described here light-scattering measurements were also carried out to ensure that we dealt with real solutions in all cases.

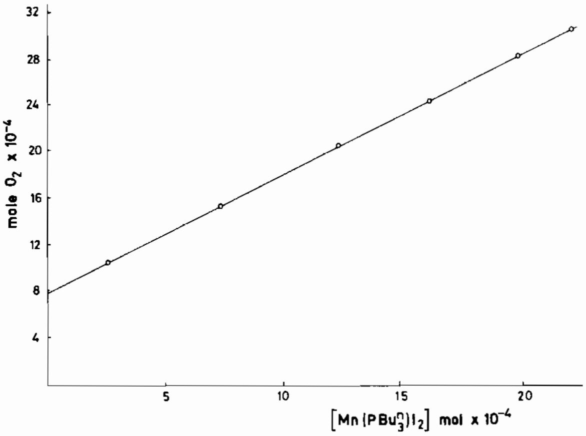

Fig. 1. Plot of dioxygen absorption as a function of complex concentration in 100 cm³ THF. Slope = 1.02; intercept = 7.8×10^{-4} mole O_2.

The equilibrium constant for binding of dioxygen

$$Mn(PR_3)X_3 + O_2 \xrightleftharpoons{k_{O_2}} Mn(PR_3)X_2{\cdot}O_2$$

can be calculated from this isotherm and by the use of the Hill equation [3–8], Fig. 2:

$$\frac{Y}{1-Y} = \frac{[Mn(PR_3)X_2{\cdot}O_2]}{[Mn(PR_3)X_2]} = K_{O_2}{\cdot}P^n_{O_2}$$

$$= (P^{O_2}_{1/2})^{-1}{\cdot}P^n_{O_2}$$

where Y is the fraction of the dioxygenated sites, K_{O_2} is the equilibrium constant for the reaction, $P_{1/2}$ is the partial pressure at half oxygenation (*i.e.* P_{O_2} at which 50% of the sites are dioxygenated).

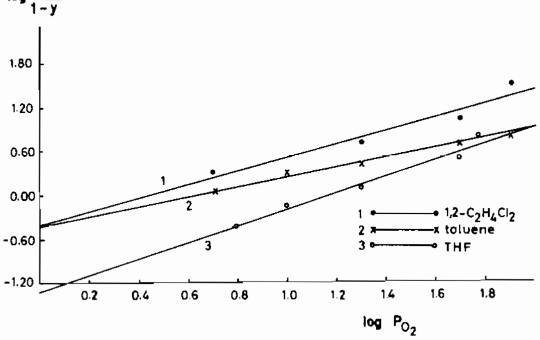

Fig. 2. Hill plots for $Mn(PBu^n_3)Br_2$ (computer assisted).

We report here equilibrium constants at 20 °C for dioxygenation of the complexes $Mn(PR_3)Br_2$ ($R_3 = Me_2Ph, Pr^n_3, Bu^n_3$) and $Mn(PPr^n_3)Cl_2$ in a number of solvents, Table I. From the isotherms for Mn-

TABLE I. Equilibrium Data for Dioxygen Uptake by $Mn(PR_3)X_2$ at 20 °C.

Complex	Solvent	log K (torr^{-1})	K_{O_2} (torr^{-1})	$P^{O_2}_{1/2}$ (torr)	Hill Coeff. n
$Mn(PBu^n_3)Br_2$	THF	–1.320	0.479×10^{-1}	20.9	1.12
	toluene	–0.429	3.72×10^{-1}	2.7	0.68
	$1,2\text{-}C_2H_4Cl_2$	–0.429	3.82×10^{-1}	2.6	0.94
$Mn(PPr^n_3)Br_2$	THF	–1.073	0.85×10^{-1}	11.8	0.86
	toluene	–0.251	5.61×10^{-1}	1.8	0.54
$Mn(PPr^n_3)Cl_2$	THF	–2.707	0.20×10^{-2}	509	1.35
	toluene	–1.565	2.72×10^{-2}	37	1.02
$Mn(PPhMe_2)Br_2$	toluene	–1.320	0.479×10^{-1}	20.9	1.12

$(PBu^n_3)Br_2$ it is readily seen that the shape and position of the curve is solvent dependent, Fig. 3. In non-coordinating solvents such as toluene or 1,2-dichloroethane the curves are strikingly reminiscent of the hyperbolic curve of myoglobin [8], whereas the shape of isotherm for tetrahydrofuran solution indicates a more complex interaction, presumably involving solvent participation.

The values of K_{O_2}, Table I, vary between 0.5×10^{-2} and 2.8×10^{-1}, and $P^O_{1/2}$ varies between 3.55 and 200 torr. These variations show the dependence of the affinity of dioxygen for these $Mn(PR_3)X_2$ complexes on (*a*) the solvent employed, (*b*) the R group on the phosphine, and (*c*) the halide, and from Table I it may be deduced that affinity for dioxygenation binding is solvent-dependent in the order $1,2\text{-}C_2H_4Cl_2$ > toluene > THF, and on changing the phosphine varies $PPr^n_3 > PBu^n_3 > PPhMe_2$.

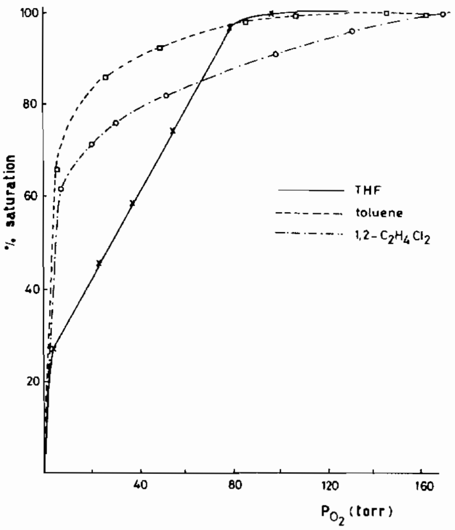

Fig. 3. Dioxygen binding curves for $Mn(PBu^n_3)Br_2$.

In Table II is listed some K_{O_2} and $P_{1/2}$ values for both natural and synthetic binders of dioxygen. From this and the Fig. 3 it can be seen that $Mn(PBu^n_3)Br_2$ in 1,2-dichloroethane is a remarkably close analogue of myoglobin.

TABLE II. Comparison of Dioxygen Affinities of Natural and Synthetic Binders.

Compound	Solvent	K_{O_2} (torr^{-1})	$P^O_{1/2}$ (torr)	Temp. (°C)	Ref.
Mb	Water	1.54	0.65	20	7,8
CoMb		1.85×10^{-2}	54	20	5
Co(TpivPP)(N-MeIm)	Toluene	7.14×10^{-1}	140	20	6
$Mn(TPP)PBu^n_3$	Toluene	3.02×10^{-9}	331×10^{-6}	−78	3,7
$Mn(PPr^n_3)Br_2$	Toluene	5.16×10^{-1}	1.8	20	this work
$Mn(PBu^n_3)Br_2$	$1,2\text{-}C_2H_4Cl_2$	3.82×10^{-1}	2.6	20	this work

References

1 (a) C. A. McAuliffe, H. Al-Khateeb, M. H. Jones, W. Levason, K. Minten and F. P. McCullough, *J. Chem. Soc. Comm.*, 736 (1979);
(b) Patent Cooperation Treaty, Application Number PCT/GB79/0038, International Publication Number WO 79/00696.

2 M. Barber, R. Bordoli, A. Hosseiny, K. Minten, C. P. Perkin, R. D. Sedgwick and C. A. McAuliffe, *Inorg. Chim. Acta*, 210 (1980), in press.

3 M. J. Carter, D. P. Rillema and F. Basolo, *J. Am. Chem. Soc.*, *96*, 392 (1974).

4 L. S. Chen, M. E. Koehler, B. C. Pestel and S. C. Cummings, *J. Am. Chem. Soc.*, *100*, 7248 (1978).

5 J. P. Collman, *Accounts Chem. Res.*, *10*, 265 (1977).

6 J. P. Collman, J. I. Brauman, K. M. Doxsee, T. R. Halbert, S. E. Hayes and K. S. Suslick, *J. Am. Chem. Soc.*, *100*, 2761 (1978).

7 R. Jones, D. A. Summerville and F. Basolo, *Chem. Rev.*, *79*, 139 (1979).

8 For the extremely lucid discussion of equilibria in dioxygen proteins see L. Stryer, 'Biochemistry', Freeman and Co., San Francisco (1975).