Oxygen Sensitive Mn(depe)$_2$X$_2$ Complexes

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In an attempt to find an attractive chemical compound for use in air separation systems, new complexes of manganese(II) halides were synthesized with various types of ligands. From the various coordinating compounds that were synthesized and tested for their oxygen affinity, MnL_2X_2 (where X = Br, NCS; L = depe = 1,2-bis(diethylphosphino)-ethane) complexes demonstrated potential for use in an oxygen separation system. The details of preparation of these compounds are reported elsewhere [1]. These compounds either in the solid state or in solution in tetrahydrofuran (THF) or toluene react with oxygen reversibly at room temperature and about atmospheric partial pressure of oxygen. A plot of oxygen reacted *versus* partial pressure of oxygen at two different temperatures is shown in Fig. 1. The oxygen reacted was measured using a volume reduction method. Details of experimental set-up and the method employed are described in a previous paper [1]. The equilibrium constants for binding of oxygen are calculated from the isotherm data using Hill's equation [2].

$$\mathrm{Mn(depe)_2X_2} + \mathrm{O_2} \rightleftharpoons \mathrm{Mn(depe)_2X_2{\cdot}O_2}$$

$$\frac{Y}{1-Y} = \frac{[\mathrm{Mn(depe)_2X_2{\cdot}O_2}]}{[\mathrm{Mn(depe)_2X_2}]} = K_{O_2}P_{O_2}{}^{n}$$

where Y is the fraction of oxygenated sites and K_{O_2} is the equilibrium constant for the reaction. Table I compares the relevant equilibrium data for oxygen uptake by these MnL_2X_2 complexes and previously reported [1, 2] $MnLX_2$ (where L = tertiary phosphine) complexes.

Kinetic studies were also conducted with MnL_2X_2 complexes coated on 3 mm diameter glass beads. Oxygen reacted was measured using the same apparatus as used in obtaining the isotherms. A plot of volume of oxygen reacted *versus* time in minutes at various temperatures is shown in Fig. 2. Further, equilibrium studies at atmospheric pressure were conducted at various temperatures and the results are plotted in Fig. 3. The results indicate that at about 18.3 °C there exists a peak temperature at which the amount of oxygen bound is maximum

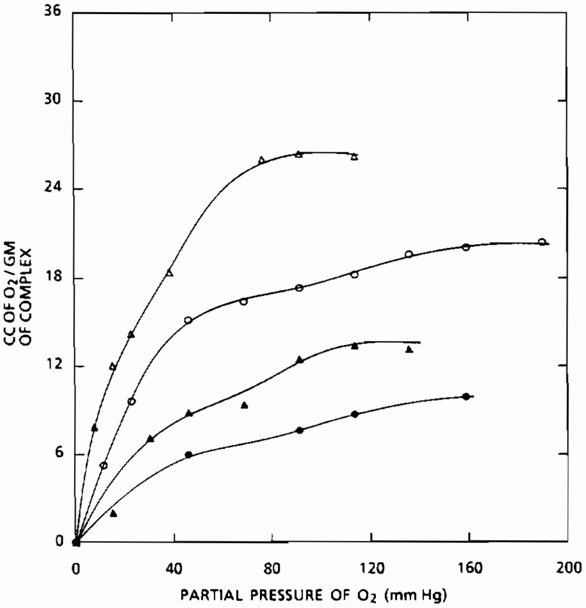

Fig. 1. Isotherms for Mn(depe)$_2$X$_2$ complexes at 760 torr total pressure. △ and ▲ = Mn(depe)$_2$Br$_2$ at 21.1 and 4.4 °C, respectively. ○ and ● = Mn(depe)$_2$(NCS)$_2$ at 21.1 and 4.4 °C, respectively.

TABLE I. Comparison of Equilibrium Data for Oxygen Uptake by Mn(depe)$_2$X$_2$ and MnLX$_2$ Complexes

Complex	Solvent	Temperature (°C)	log K_{O_2} (Torr^{-1})	n	Reference
Mn(depe)$_2$Br$_2$		21.1	−1.486	1.11	this work
		4.4	−2.225	0.95	this work
Mn(depe)$_2$(NCS)$_2$		21.1	−2.086	1.40	this work
		4.4	−2.434	0.81	this work
Mn(PBu$^n_3$)Br$_2$	THF	20	−1.32	1.12	2
Mn(PPr$^n_3$)Cl$_2$	THF	20	−2.71	1.35	2
Mb	water	20	0.187		3

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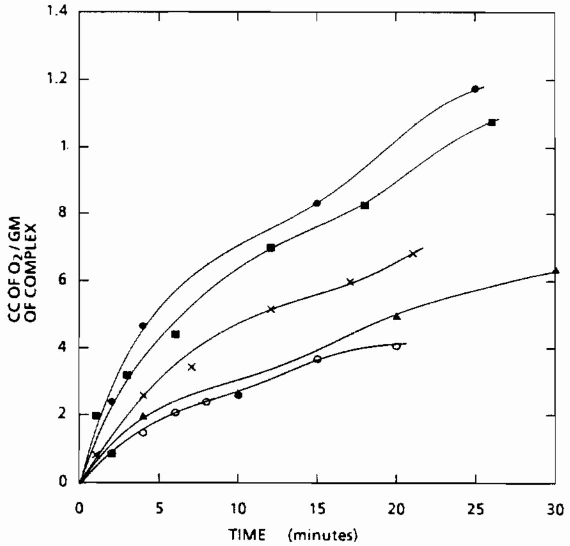

Fig. 2. Kinetic data for $Mn(depe)_2(NCS)_2$ at 21% O_2 and 14.7 psi. ○, ●, ■, ×, ▲ = 4.4, 21.1, 26.6, 32.2, 43.3 °C, respectively.

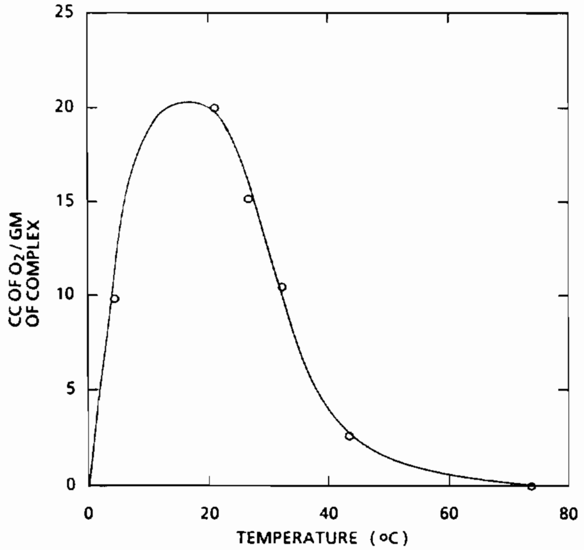

Fig. 3. Equilibrium data for $Mn(depe)_2(NCS)_2$ at various temperatures, 21% O_2 and 14.7 psi.

and as the temperature is increased further there is a reduction of oxygenation by the complex. The complex is finally incapable of oxygenation at about 74 °C. Samples of $Mn(depe)_2(NCS)_2$–THF solutions show similar results, except that the rate of reaction with oxygen is higher. The requirement of longer time for the complex to reach equilibrium in the solid state is expected since mass transfer effects are more pronounced with a solid complex in a static system. However, an important point to be realized is that by cycling the temperature between favorable sorption and desorption temperatures, these chemicals can be optimized to produce oxygen or oxygen enriched air.

Suitable crystals of the bromo derivative were isolated and studied using X-ray diffraction [3]. This has confirmed that the reaction of $MnBr_2$ with depe is indeed a 1:2 adduct, *i.e.* *trans*-dibromobis(diethylphosphino)ethanemanganese(II), *trans*-$Mn(depe)_2Br_2$ with Mn(II) occupying a unique position. There are no unusual distortions in the molecular geometry of this octahedral complex. The metal–ligand distances are within the range expected for high-spin d^5 six-coordinated Mn(II) compounds. The final Mn–P distances are 2.697(1) and 2.720(1) Å with the final Mn–Br distance of 2.649(1) Å. In contrast, an opposite trend is observed in *trans*-$Mn(dmpe)_2Br_2$, where the Mn–P distance [2.655(4) Å] is found to be slightly shorter than the Mn–Br distance [2.666(3) Å] [4]. This reversal is entirely consistent with standard stearic and electronic concepts. The ethyl groups in depe (being spatially and stearically more demanding than the methyls in dmpe) are direct contributors to an increase in interligand repulsions which is relieved through an increase in the Mn–P distances. Consequently, Mn–P π-backbonding is lowered, accompanied by strengthening of the Mn–Br bond, and a shortening in the Mn–Br distance. Finally, a smaller P–Mn–P bite angle is observed in the dppe complex [77.5(1)° *versus* 78.8(1)° for the dmpe analogue] as would be expected to accompany the presence of longer Mn–P bonds.

Further studies on these and other similar complexes are in progress at the laboratory with potential applications to the separation of gases from mixtures [3].

Supplementary Material

Details of X-ray crystallographic data for $Mn(depe)_2Br_2$ are available from the authors upon request.

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