# Thermodynamic and Kinetic Studies on the Reaction of Sulphur Dioxide with Manganese(II) Phosphine Oxide Complexes

GEORGE A. GOTT, CHARLES A. McAULIFFE* and PHILOMENA P. MacRORY

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

(Received September 19, 1989)

## Abstract

The bonding of sulphur dioxide to $Mn(OPPh_3)_4X_2$ (X = NCS or I) in the solid state has been studied using a gas burette; thermodynamic data obtained indicate that the binding of sulphur dioxide is weak, and kinetic data for the reaction of sulphur dioxide with $Mn(OPPh_3)_4(NCS)_2$ indicate a two stage reaction, both of which obey pseudo first order kinetics.

There is an increasing interest in the interaction of transition metal complexes with sulphur dioxide [1], and we have recently reported the binding of sulphur dioxide to $Mn(OPPh_3)_4I_2$ [2] and $Mn(OAsPh_3)_4I_2$ [3]. In the case of $Mn(OPPh_3)_4I_2$ two moles of $SO_2$ are bound per manganese via an insertion reaction to give $Mn(OPPh_3)_4(OSOI)_2$, whereas with $Mn(OAsPh_3)_4I_2$ two moles of $SO_2$ are bound, together with the loss of a $OAsPh_3$ ligand, to give $Mn(OAsPh_3)_3(OSOI)_2$. We now wish to report some preliminary thermodynamic and kinetic studies on the reaction of sulphur dioxide with $Mn(OPPh_3)_4X_2$ (X = I or NCS).

The apparatus employed consisted of a gas burette connected to a reaction vessel (containing a powdered sample of the complex under investigation) via a 2 l reservoir immersed in a constant temperature bath. The whole apparatus was evacuated, filled with a sulphur dioxide–argon mixture of known composition, and the volume of sulphur dioxide absorbed by the complex measured with the gas burette. This enabled absorption curves to be constructed at different temperatures which are shown in Figs. 1 and 2.

The curves show several interesting features. For $Mn(OPPh_3)_4(NCS)_2$ a plateau is reached at *c.* 1:1 absorption at all the temperatures studied, which is in agreement with other work that has shown the formation of a 1:1 adduct in the solid state and in toluene slurries [4]. With $Mn(OPPh_3)_4I_2$ the curves indicate that above room temperature there is little tendency for a second $SO_2$ molecule to bind, and that at the higher partial pressures of sulphur dioxide

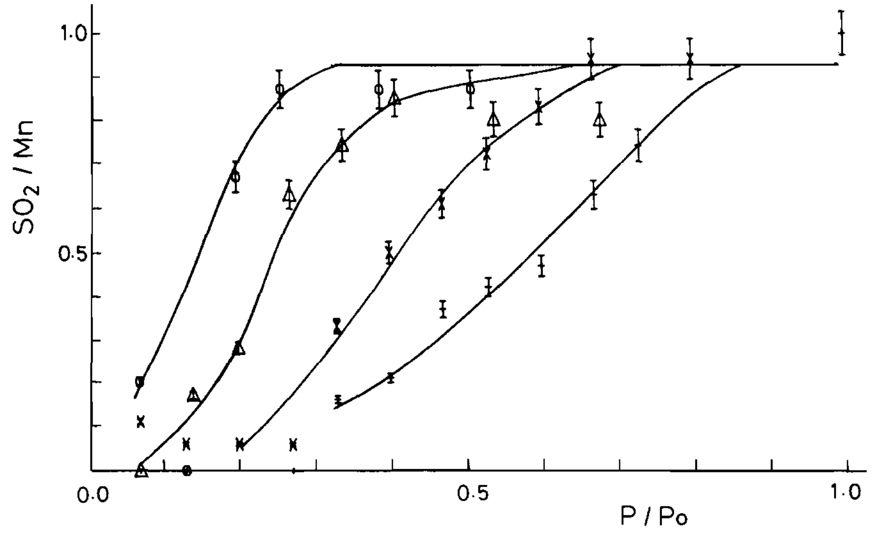

Fig. 1. Absorption of $SO_2$ by $Mn(OPPh_3)_4(NCS)_2$ at 19 °C (○), 35 °C (△), 57 °C (×), 74 °C (+).

---

*Author to whom correspondence should be addressed.

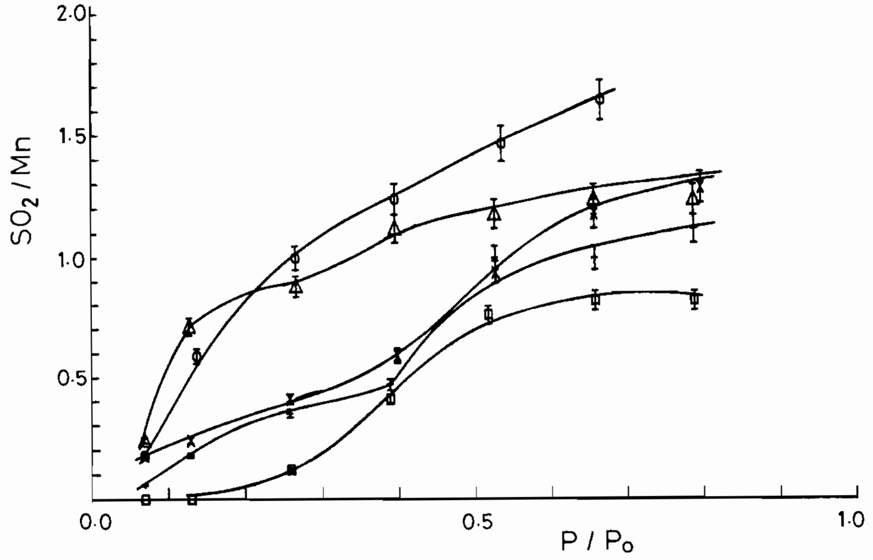

Fig. 2. Absorption of $SO_2$ by $Mn(OPPh_3)_4I_2$ at 21 °C (○), 34 °C (△), 43 °C (×), 56 °C (+), 72 °C (□).

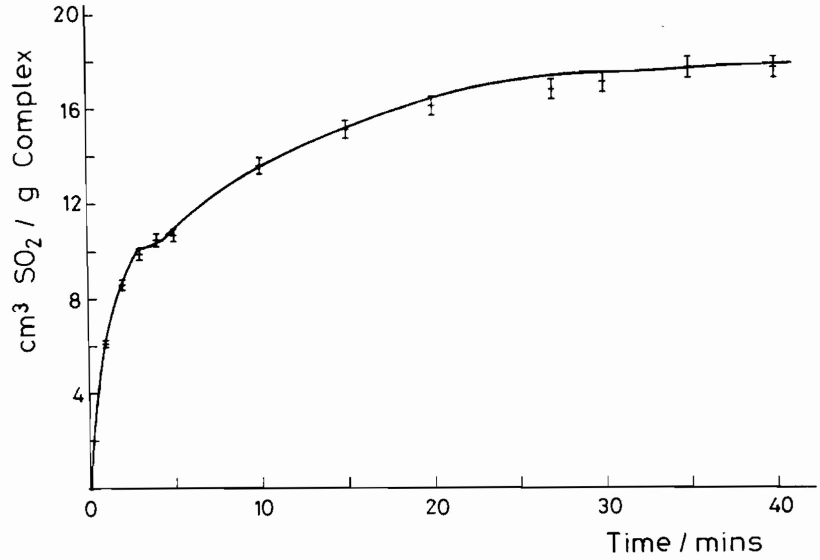

Fig. 3. Uptake of $SO_2$ by $Mn(OPPh_3)_4(NCS)_2$ with time at 19 °C.

TABLE 1. Dissociation enthalpies for $Mn(OPPh_3)_4X_2(SO_2)_n$

| Saturation (%) | Dissociation enthalpy (kJ $mol^{-1}$) | |
|---|---|---|
| | $Mn(OPPh_3)_4(NCS)_2(SO_2)$ | $Mn(OPPh_3)_4I_2(SO_2)_n$ |
| 10 | 32.4 | 25.8 |
| 20 | 26.6 | 21.5 |
| 30 | 24.1 | 20.3 |
| 40 | 21.9 | 17.6 |
| 50 | 21.2 | 22.0 |

the affinity for sulphur dioxide is the same at 43 °C as at 34 °C. This may be due to a phase change which occurs around this temperature [4].

Dissociation enthalpies for the sulphur dioxide adducts were calculated from the Clausius Clapeyron equation

$$\frac{d(\ln P)}{d(1/T)} = \frac{-\Delta H}{R} \qquad \Delta H = \text{enthalpy of dissociation}$$

Dissociation enthalpies calculated are shown in Table 1. The values of $\Delta H$ obtained are relatively small, c. 20 kJ $mol^{-1}$, and are similar to the dissociation enthalpies of c. 36–60 kJ $mol^{-1}$ for the complexes $Cu_2(PR_3)_4I_2(SO_2)$ [5] and c. 14 kJ $mol^{-1}$ for the complex ion $(NCS \cdot SO_2)^-$ [6], previously reported. The low dissociation enthalpies are indicative of weak bonding in the adducts and this is reflected in the ease of loss of sulphur dioxide from $Mn(OPPh_3)_4(NCS)_2(SO_2)$, which releases sulphur dioxide readily when not under a sulphur dioxide atmosphere [4].

The reaction of sulphur dioxide ($P = 1$ atm.) with $Mn(OPPh_3)_4(NCS)_2$ with time has also been studied using the same apparatus. A typical uptake curve is shown in Fig. 3. Again saturation is reached with the formation of a 1:1 adduct. Initial uptake is rapid with c. 50% saturation being reached after c. 4 min. This is followed by a slower phase, and complete reaction is attained after c. 35 min. The data correspond to pseudo first order kinetics for both phases of the reaction, with rate constants of $40.0 \times 10^{-4}$ and $3.0 \times 10^{-4}$ $s^{-1}$ at 19 °C.

## References

1 W. R. Scheidt, Y. J. Lee and M. G. Finnegan, *Inorg. Chem.*, *27* (1988) 4725.

2 J. Fawcett, G. A. Gott, C. A. McAuliffe and D. R. Russell, *J. Chem. Soc., Chem. Commun.*, (1984) 1283.

3 C. A. McAuliffe, B. Beagley, G. A. Gott, A. G. Mackie, P. P. MacRory and R. G. Pritchard, *Angew. Chem., Int. Ed. Engl.*, *26* (1987) 264.

4 O. El-Sayrafi, G. A. Gott, C. A. McAuliffe, P. P. MacRory and R. G. Pritchard, unpublished work.

5 P. G. Eller, G. J. Kubas and R. R. Ryan, *Inorg. Chem.*, *17* (1977) 2545.

6 S. Wasif and S. B. Salama, *J. Chem. Soc., Dalton Trans.*, (1973) 2148.