

Thermodynamic studies on the reaction of sulfur dioxide with $[\text{Mn}(\text{vppO}_2)_2(\text{NCS})_2]$ ($\text{vppO}_2 = \text{cis-Ph}_2\text{P}(\text{O})\text{CHCHP}(\text{O})\text{Ph}_2$)

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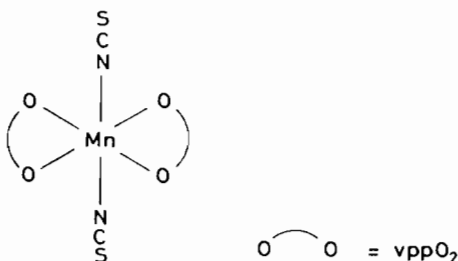
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Abstract

The reaction of sulfur dioxide with $\text{Mn}(\text{vppO}_2)_2(\text{NCS})_2$ ($\text{vppO}_2 = \text{cis-Ph}_2\text{P}(\text{O})\text{CHCHP}(\text{O})\text{Ph}_2$) in the solid state leads to the production of the adduct $\text{Mn}(\text{vppO}_2)_2(\text{NCS})_2 \cdot \text{SO}_2$. The equilibrium constant for this process has been studied over a range of temperatures; the mean standard enthalpy for the process is $-156.1 \text{ kJ mol}^{-1}$, indicative of chemisorption.

Interest in the coordination of sulfur dioxide to transition metal complexes has been increasing, particularly in view of the environmental hazards associated with sulfur dioxide. We have recently reported some preliminary thermodynamic studies on the reaction of sulfur dioxide with manganese(II) phosphine oxide complexes [1]. We now wish to extend this to include a diphosphine dioxide complex, $\text{Mn}(\text{vppO}_2)_2(\text{NCS})_2$, which absorbs one mole of SO_2 per mole of complex at room temperature.

This novel complex was prepared by reacting anhydrous manganese(II) thiocyanate with a slight excess of the theoretically required amount of vppO_2 (obtained by stirring vpp [2] with H_2O_2 in hot acetone for *c.* 3 h) in freshly distilled toluene under an argon atmosphere. The reactants were stirred for 10 days at room temperature and the product was isolated by standard Schlenk techniques. *Anal.* Calc. for $\text{Mn}(\text{vppO}_2)_2(\text{NCS})_2$: C, 63.1; H, 4.3; N, 2.4; S, 5.8. Found: C, 63.1; H, 4.3; N, 2.7; S, 6.2%. A nujol mull IR spectrum exhibited bands at $1170, 1160 \text{ cm}^{-1}$ assignable to $\nu(\text{PO})$ and at 2060 cm^{-1} to $\nu(\text{CN})$. The single $\nu(\text{CN})$ band strongly suggests a *trans* arrangement of the thiocyanates, viz.



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The apparatus employed for the thermodynamic study consisted of a gas burette connected to a reaction vessel (containing a powdered sample of the complex) via a 3 l mixing-bulb immersed in a constant temperature bath. The whole apparatus was evacuated, filled with an initial SO_2 -Ar mixture of known composition, and the volume of SO_2 absorbed by the complex measured using the gas burette. The P_{SO_2} was increased in stages and the volume changes recorded correspondingly. This enabled the number of moles of SO_2 absorbed at a given temperature and pressure to be calculated, and hence absorption curves to be drawn, Fig. 1.

The curves indicate that saturation is obtained at each temperature point. However, although the absorption of SO_2 increases with increasing SO_2 pressure, it decreases with increasing temperature, e.g. at 15°C a 1:1 Mn: SO_2 adduct is formed but at 35°C only 0.7 mol of SO_2 are absorbed per Mn. This is not unexpected since absorption involves a decrease in both entropy and free energy. From the thermodynamic relationship

$$\Delta G = \Delta H - T\Delta S$$

it is evident that ΔH must be negative, i.e. the adsorption of gases on solids is always an exothermic process. The effect of increasing the temperature can be predicted using Le Chatelier's Principle. However, this gives only a qualitative indication of the direction in which an equilibrium is displaced by a rise in temperature.

A quantitative relationship between the heat of the reaction and the change in the equilibrium constant is given by the van't Hoff isochore [3]

$$\frac{d \ln K_{\text{eq}}}{dT} = \frac{\Delta H_{\text{M}}^\circ}{RT^2}$$

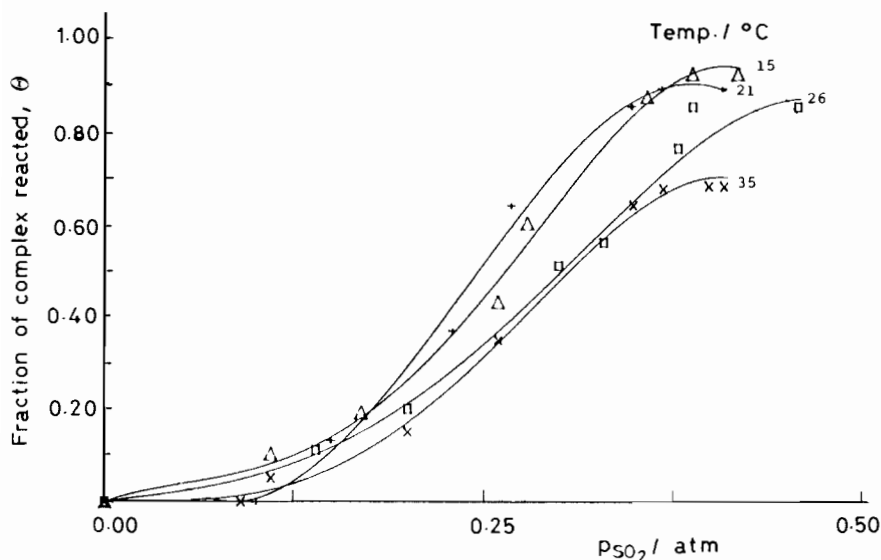
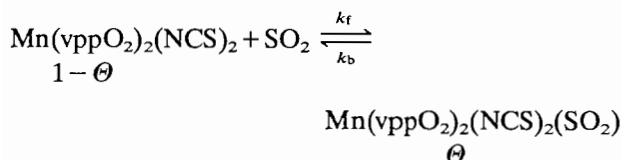


Fig. 1. Combined isotherms at $T=15, 21, 26$ and 35 °C for the reaction of $\text{Mn}(\text{vppO}_2)_2(\text{NCS})_2$ with sulfur dioxide.

It was assumed that the interaction between SO_2 and $\text{Mn}(\text{vppO}_2)_2(\text{NCS})_2$ results in a monolayer formation of the SO_2 adduct and that SO_2 absorption and, consequently, its reaction with the complex is independent of the presence or absence of the nearby reaction sites. The model employed for this reaction is as follows:

If θ represents the fraction of surface already reacted then $(1-\theta)$ is the fraction unreacted.



Rate of forward reaction, $R_f \propto P_{\text{SO}_2}$
 $\propto (1-\theta)$

i.e. $R_f \propto P_{\text{SO}_2}(1-\theta)$
 and $R_f = k_f P_{\text{SO}_2}(1-\theta)$

At the same time,

rate of reverse reaction, $R_b \propto \theta$
 and $R_b = k_b \theta$

At equilibrium $R_f = R_b$, i.e. $k_f P_{\text{SO}_2}(1-\theta) = k_b \theta$

$$\text{Therefore } \theta = \frac{K_{\text{eq}} P_{\text{SO}_2}}{(K_{\text{eq}} P_{\text{SO}_2} + 1)} \quad (1)$$

Equation (1) shows that when $P_{\text{SO}_2} = 0$, $\theta = 0$ and when P_{SO_2} is large, $\theta = 1$. This equation accounts for the S-shaped nature of the absorption isotherms.

The fraction of reacted sites is proportional to the number of moles of SO_2 ,

i.e. $\theta \propto n\text{SO}_2$

$$\theta = Kn\text{SO}_2$$

(where K is a function of moles of $\text{Mn}(\text{vppO}_2)_2(\text{NCS})_2$ present in the solid, $K = f(n\text{Mn})$.)

Thus substituting $Kn\text{SO}_2$ for θ in eqn. (1)

$$Kn\text{SO}_2 = \frac{K_{\text{eq}} P_{\text{SO}_2}}{(K_{\text{eq}} P_{\text{SO}_2} + 1)}$$

$$\frac{1}{n\text{SO}_2} = K + \frac{K}{K_{\text{eq}}(P_{\text{SO}_2})} \quad (2)$$

A plot of $1/n\text{SO}_2$ versus $1/P_{\text{SO}_2}$ yields a straight line with slope K/K_{eq} and intercept, K . Hence the equilibrium constant, K_{eq} , for that particular temperature can be estimated, Table 1.

Having established the K_{eq} value for each temperature, the molar heat of reaction between $\text{Mn}(\text{vppO}_2)_2(\text{NCS})_2$ and SO_2 can be calculated from the van't Hoff isochore [3].

The integrated form of this equation is

$$\ln K_{\text{eq}} = \frac{-\Delta H_{\text{M}}^\circ}{RT} + \text{constant}$$

A plot of $\log_{10} K_{\text{eq}}$ versus $1/T$ (Fig. 2) has slope $\Delta H_{\text{M}}^\circ / 2.303R$, where $\Delta H_{\text{M}}^\circ$ is the mean standard enthalpy of the reaction

TABLE 1. Equilibrium constants at various temperatures

Temperature (K)	$10^5 \times K_{\text{eq}}/\text{atm}$
288	2.29
294	1.87
299	0.25
308	0.047

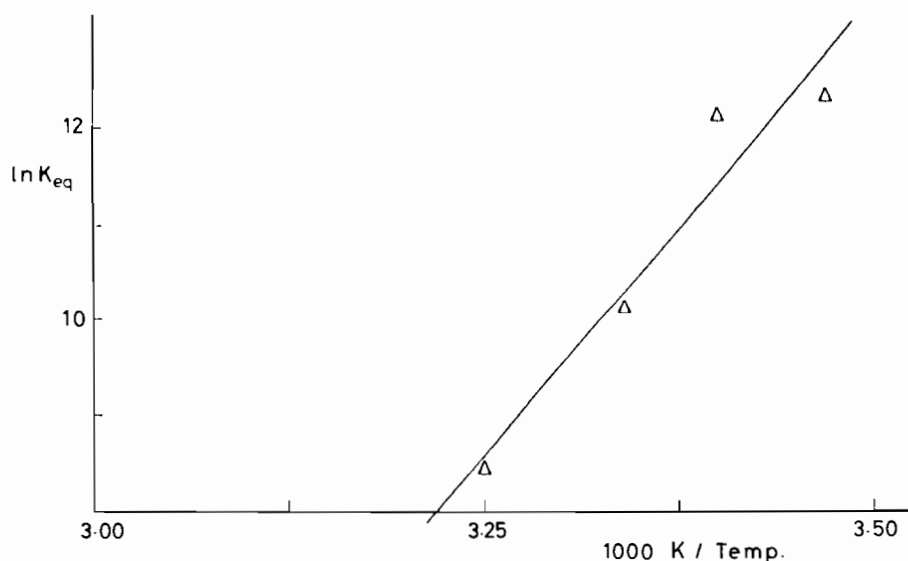
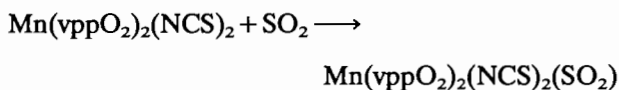


Fig. 2. The van't Hoff isochore for the reaction of $\text{Mn}(\text{vppO}_2)_2(\text{NCS})_2$ with sulfur dioxide.



This is found to be $-156.1 \text{ kJ mol}^{-1}$, close to the values expected for chemisorption (-200 kJ mol^{-1}).

The energy of attachment of the SO_2 here is very much greater than that found in our previous work, c. 20 kJ mol^{-1} [1]. It is also more strongly bound than in $\text{Cu}_2(\text{PR}_3)_4\text{I}_2(\text{SO}_2)$ ($36\text{--}60 \text{ kJ mol}^{-1}$) [4] or $(\text{NCS} \cdot \text{SO}_2)^-$ (14 kJ mol^{-1}) [5]. So, whilst the reaction of $\text{Mn}(\text{vppO}_2)_2(\text{NCS})_2$ with SO_2 is reversible, the SO_2 is relatively firmly held and is more difficult to remove than, for example, in the reaction of $\text{Mn}(\text{OPPh}_3)_4(\text{NCS})_2 + \text{SO}_2$ [6].

The structure of the SO_2 adduct is, at present, unconfirmed. The insertion of the SO_2 into one of the Mn–NCS bonds, analogous to the crystallographically characterised $[\text{Mn}(\text{OPPh}_3)_4\{\text{OS}(\text{O})\text{I}\}_2]$ [7], might be expected to result in two $\nu(\text{CN})$ absorptions. However, whilst the IR spectrum of the SO_2 adduct does exhibit a new absorption at 2050 cm^{-1} , it is only a single peak; the original $\nu(\text{CN})$ in the $[\text{Mn}(\text{vppO}_2)_2(\text{NCS})_2]$ at 2060 cm^{-1} has disappeared. It seems more likely that the SO_2 is ligand-bound. Ligand-bound SO_2 is well established [8–10] and is generally characterised by revers-

ibility and unreactivity towards dioxygen. Both of these criteria are met here.

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