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Spectrophotometric Detection of Sulfur Dioxide: a Study of the Solution Equilibria of the Reaction of Sulfur Dioxide with Manganese(II) Complexes

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Abstract

Spectrophotometric detection of sulfur dioxide binding by certain manganese(II) complexes in tetrahydrofuran solutions can be followed by monitoring changes in the electronic spectra. Solution isotherms have been constructed and from these the affinity of these complexes towards sulfur dioxide follows the order: $Mn(Ph_3PO)_2I_2 > Mn(Ph_3PS)_2I_2 > Mn(Ph_3AsO)_2I_2$; $Mn(Ph_3PS)_4I_2 > Mn(Ph_3PO)_4I_2 > Mn(Ph_3AsO)_4I_2$; $Mn(dpeO_2)_2I_2 > Mn(dpeS_2)_2I_2$ [$Ph_2P(Y)CH_2CH_2P(Y)Ph_2$; Y = O, $dpeO_2$; Y = S, $dpeS_2$]; and $MnL_4I_2 > MnL_2I_2$ for the monodentate ligands.

Introduction

We have previously reported the reaction of certain manganese(II) complexes of triphenylphosphine oxide and triphenylarsine oxide with sulfur dioxide [1–5] and some interesting structure/reactivity trends have emerged already. Thus, for example, the tris and tetrakis triphenylphosphine oxide complexes of manganese(II) thiocyanate react reversibly with SO_2 to give 1:1 adducts $[Mn(OPPh_3)_n(NCS)_2(SO_2)]$ ($n = 3, 4$), although the mono and bis ligand complexes are inactive. Moreover, as well as binding sulfur dioxide the manganese complexes activate it. For example, dilute solutions of $[Mn(OPPh_3)_4(NCS)_2(SO_2)]$ in the presence of air allow the oxidation of sulfur dioxide to sulfuric acid, as evidenced by the isolation and X-ray crystallographic characterisation of $[(Ph_3PO)(Ph_3POH)HSO_4]$ [5]. We now wish to report an investigation of the reaction of sulfur dioxide with some manganese(II) complexes in solution. Such reactions frequently cause a marked colour change and this therefore seems a reasonable basis on which to develop a method of detection and analysis for sulfur dioxide using visible spectrophotometry. The method employed is based on the variation of the electronic spectra of the manganese(II) complexes with the partial pressure of sulfur dioxide, P_{SO_2}. It has been possible to construct SO_2-binding curves (isotherms) and from these to compare the affinities of the complexes for SO_2.

Results and Discussion

Manganese(II) iodide complexes showed most potential in the spectrophotometric investigation. The complexes employed were MnL_nI_2 ($L = Ph_3PO$, Ph_3AsO, Ph_3PS, $n = 2, 4$; $L = dpeO_2$, $dpeS_2$, $n = 2$); these were prepared as described in 'Experimental'. Initially each complex was dissolved in THF, its UV–Vis spectrum was recorded and λ_{max} and ϵ (molar absorptivity) were determined, Table 1. Upon exposure to sulfur dioxide the electronic spectra of these complexes displayed intense absorption bands within the same region. Since the spectra of the SO_2-treated solutions and the spectra of the SO_2-free solutions are to be compared, employing solutions of the same concentrations ensures that any increase in the intensity of the absorption can be attributed to the effect of sulfur dioxide coordination. Examples of the spectra obtained are given in Fig. 1.

By following the increase in the intensity of the electronic spectra with increasing partial pressure of sulfur dioxide plots of ϵ_{max} versus P_{SO_2} can be drawn

TABLE 1. λ_{max} and molar absorptivity for manganese(II) complexes in THF

Complex	λ_{max} (nm)	ϵ_{max} ($l\ mol^{-1}\ cm^{-1}$)
$Mn(Ph_3PO)_4I_2$	360–362	1269
$Mn(Ph_3PO)_2I_2$	365	1975
$Mn(Ph_3AsO)_4I_2$	365	740
$Mn(Ph_3AsO)_2I_2$	365	3000
$Mn(Ph_3PS)_4I_2$	345	225
$Mn(Ph_3PS)_2I_2$	325	552
$Mn(dpeO_2)_2I_2$	325	6876
$Mn(dpeS_2)_2I_2$	325	1118

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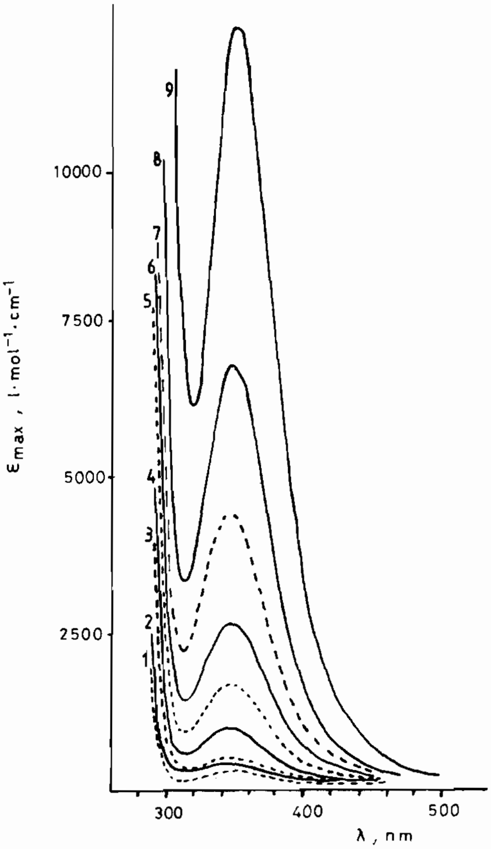

Fig. 1. Variation of electronic spectrum with P_{SO_2} for $Mn(Ph_3AsO)_2I_2$ in THF at room temperature: 1, 5; 2, 10; 3, 20; 4, 60; 5, 120; 6, 200; 7, 300; 8, 450; 9, 600 Torr.

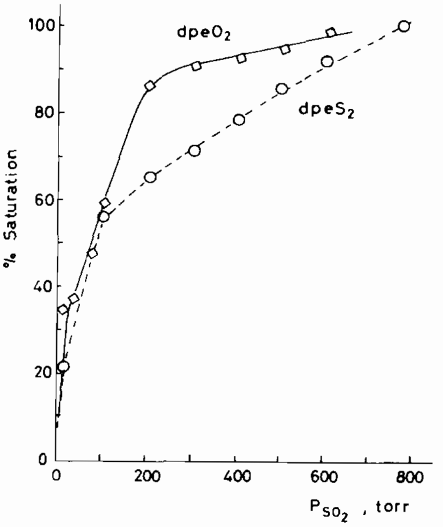

Fig. 2. SO_2-binding isotherms for MnL_2I_2 (L = $dpeO_2$, $dpeS_2$) in THF at room temperature.

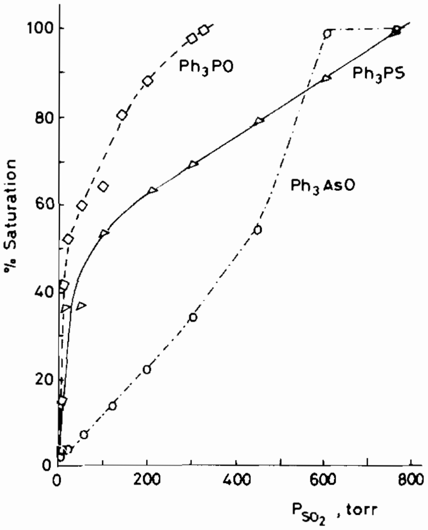

Fig. 3. SO_2-binding isotherms for MnL_2I_2 (L = Ph_3PO, Ph_3AsO, Ph_3PS) in THF at room temperature.

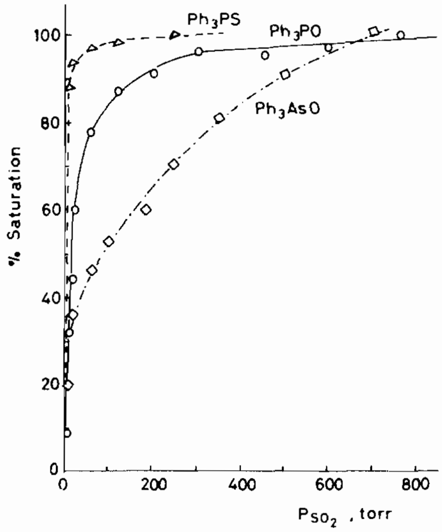

Fig. 4. SO_2-binding isotherms for MnL_4I_2 (L = Ph_3PS, Ph_3PO, Ph_3AsO) in THF at room temperature.

which show that 100% saturation is achieved for $Mn(Ph_3AsO)_2I_2$ and that $Mn(Ph_3PO)_4I_2$ and $Mn(Ph_3PS)_4I_2$ are close to 100% saturation. The remaining complexes show slightly ascending plateaus, and so to construct their solution isotherms the 100% saturation pressure was taken as the highest pressure in the plateaus. Saturation percentage is usually calculated from the ratio of the absorption intensity at λ_{max} at any P_{SO_2} relative to that of 100% saturation.

From the solution isotherms (plots of % saturation versus P_{SO_2}) trends in the affinity of the complexes for SO_2 can be observed (Figs. 2–4). A comparison of those complexes containing diphosphine derivative ligands, i.e. $Mn(dpeO_2)_2I_2$ and $Mn(dpeS_2)_2I_2$, shows that the isotherm of the diphosphine dioxide complex lies further to the left, indicative of a higher affinity for SO_2. Moreover, this complex reaches 100% saturation at a lower pressure than its phosphine sulfide analogue, Fig. 2.

The isotherms of the bis complexes $Mn(Ph_3PO)_2I_2$, $Mn(Ph_3PS)_2I_2$ and $Mn(Ph_3AsO)_2I_2$ show a somewhat similar behaviour (Fig. 3). The curve of the phosphine oxide complex is further to the left, followed by the curve of the phosphine sulfide complex, while the isotherm of the arsine oxide complex lies further to the right. However, the isotherm of the arsine oxide and phosphine sulfide complexes have a cross-over point at 540 Torr above which 100% saturation is attained for $Mn(Ph_3AsO)_2I_2$. Thus the relative affinity for SO_2-binding at $P_{SO_2} < 540$ Torr for the bis complexes appears to follow the order $Mn(Ph_3PO)_2I_2 > Mn(Ph_3PS)_2I_2 > Mn(Ph_3AsO)_2I_2$.

However, the general trend exhibited by the tetrakis complexes is different to that described above for the bis complexes. Here the phosphine sulfide complex has the lowest saturation pressure (and hence the greatest affinity for sulfur dioxide), the arsine oxide complex has the highest saturation pressure whilst the phosphine oxide complex is intermediate between the two. Again there is a cross-over point (640 Torr) but below this the affinity for SO_2 follows the order described above, i.e. $Mn(Ph_3PS)_4I_2 > Mn(Ph_3PO)_4I_2 > Mn(Ph_3AsO)_4I_2$.

Attempts to obtain equilibrium constants for the binding of SO_2 by these complexes in solution have proved difficult. Analysis of the data based on either the Hill equation [6, 7] or on a mathematical approach developed by Drago *et al.* [8, 9] and modified by Collman *et al.* [6] have been inconclusive. Previous work by us [5] suggests that in the solid state or in toluene slurries the reaction is based on a single equilibrium of the general type

$$\text{Mn complex} + SO_2 \longrightarrow SO_2 \text{ adduct}$$

However, several of the curves obtained do not fit a single equilibrium of the kind. Discontinuities are observed which can be described by more than one equilibrium. Moreover, the curves for MnL_2I_2 ($L = dpeO_2$, $dpeS_2$, Ph_3PS) all show an initial fast rise followed by a slower (almost linear) rise which again is not compatible with a single equilibrium.

Despite these difficulties, however, the relative affinity towards sulfur dioxide for each series of complexes has been determined from the solution isotherms. Thus $Mn(Ph_3PS)_4I_2 > Mn(Ph_3PO)_4I_2 > Mn(Ph_3AsO)_4I_2$; $Mn(Ph_3PO)_2I_2 > Mn(Ph_3PS)_2I_2 > Mn(Ph_3AsO)_2I_2$; and $Mn(dpeO_2)_2I_2 > Mn(dpeS_2)_2I_2$.

Experimental

Preparation of Complexes

$Mn(Ph_3PO)_2I_2$ was prepared by mixing anhydrous manganese(II) iodide (2.72 g, 8.8 mmol) with triphenylphosphine oxide (5.38 g, 19.4 mmol) in a 1:2.2 ratio in acetone at 0 °C. The solid product was filtered, washed with acetone and dried *in vacuo* over P_2O_5. $Mn(Ph_3AsO)_2I_2$ was prepared as above, but hot ethanol was used as the solvent.

$Mn(Ph_3PS)_nI_2$ ($n = 2, 4$) and MnL_2I_2 ($L = dpeO_2$, $dpeS_2$) were prepared by stirring a suspension of anhydrous MnI_2 and the required amount of ligand in toluene at room temperature under anaerobic conditions for two weeks. The solid complex was then isolated using standard Schlenk techniques.

MnL_4I_2 complexes ($L = Ph_3PO$, Ph_3AsO) were prepared by stirring the reactants in acetone at −8 °C for 30 min. The reaction mixture was kept at 0 °C overnight when the solid product was filtered, washed with cold acetone and dried over P_2O_5.

Elemental analyses were performed by the UMIST microanalytical service.

Spectrophotometric Measurements

The solution electronic spectra were recorded using 1 cm path length silica cells on a Cary 210 spectrophotometer.

All the glassware used was oven-dried and then cooled in an argon atmosphere. The appropriate amount of complex was weighed into a pre-dried argon filled volumetric flask and the dry, degassed solvent was also added to the flask in a dry-box under argon. The solutions were approximately 10^{-4} M.

A special UV-gas cell, fitted with a stopper and a side-inlet, was filled with argon and transferred to a dry-box. The cell was filled with the solution under investigation, and the spectrum of the solution was recorded against the solvent. The gas cell was then evacuated, a known pressure of SO_2 was admitted (measured on a mercury manometer) and the pressure was made up to 1 atm. with argon*. The cell was then transferred to the spectrophotometer and the spectrum recorded against SO_2-free solution of the complex in the reference compartment. The process was repeated to cover a range of SO_2 pressures (4–760 Torr).

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*In each case the top of the UV cell was opened to the gas mixture for 10 min to ensure that equilibrium was attained.

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