THE INTERACTION OF COMPLEXES MN(PPHME2)Br2 AND MN(PET3)Br2 WITH SULFUR DIOXIDE(U) AUBURN UNIV AL DEPT OF CHEMISTRY W E HILL ET AL. 18 JUL 85
The interaction of complexes \( \text{Hn} \left( \text{PPhMe}_2 \right) \text{Br}_2 \) and \( \text{Hn} \left( \text{PBr}_3 \right) \text{Br}_2 \) with sulfur dioxide

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Abstract

The interactions of the complexes \( \text{Hn} \left( \text{PPhMe}_2 \right) \text{Br}_2 \) and \( \text{Hn} \left( \text{PBr}_3 \right) \text{Br}_2 \) as films with \( \text{SO}_2 \) and \( \text{S}_2 \text{O}_3 \) have been investigated using infrared spectroscopy as an analytical probe. It is clear from these preliminary studies that two types of complexes with \( \text{SO}_2 \) have been formed. When the \( \text{HnBr}_2 \) films were exposed to low pressures of \( \text{SO}_2 \) for relatively short times, an \( \text{HnBr}_2 / \text{SO}_2 \) complex formed reversibly in that the \( \text{SO}_2 \) could be removed by prolonged evacuation. On the other hand, lengthy exposure of the \( \text{HnBr}_2 \) films to higher pressures of \( \text{SO}_2 \) caused the irreversible formation of a complex having stoichiometry \( \text{HnBr}_2 \cdot 1/2 \text{SO}_2 \). It is probable that the \( \text{SO}_2 \) bonds in some type of bridging fashion in both of the types of \( \text{HnBr}_2 / \text{SO}_2 \) complexes.
There has been considerable recent interest in complexes of the form MnsE₂ (M=tertiary phosphine, X=amine) and their interaction with dioxogen.¹,² Infrared work in these laboratories concerning films of the complexes has shown that the complexes do exist and that some do interact reversibly with dioxogen, the extent of which is markedly dependent upon the nature of the tertiary phosphine ligand.³,⁴ All of the complexes studied here, however, exhibit competing irreversible decay channels at room temperature to the corresponding phosphine oxide complexes.³,⁴ The purpose of this note is to report infrared data concerning the interaction of the complex films with sulfur dioxide.

The complex films studied here were prepared by sublimation of MnBr₂ onto a KBr infrared window followed by heating to ca. 473 K in a specially designed infrared cell³,⁴ at 10⁻⁶ Torr to remove all water. Then the dry MnBr₂ films were exposed to either PF₅Me₄ or Ph₅P₃ or Plex to form the MnL₂ complex films. Extensive evacuation at 10⁻⁶ Torr was employed to remove all traces of excess phosphine. The films thus prepared were exposed to SO₂/excavation cycles with infrared spectra (Perkin-Elmer Models 380 or 983 with data station) being monitored at appropriate intervals. Since SO₂(g) exhibits infrared bands near 520, 1150, and 1360 cm⁻¹ which might have interfered with resolution of the complex bands, the cell was always briefly evacuated following SO₂ exposure immediately before infrared analysis.

Figure 1 shows the infrared spectra corresponding to the Mn(PF₅Me₄)Br₂ complex film interacting with SO₂. A comparison of Fig. 1b and 1a reveals that new infrared bands at SO₂(g¹⁸O₂): 412(410), 445(440), 525(515), 785(780), 995(950), 1002(968), and 1075(1038) cm⁻¹ appear which can be attributed to a new complex(es) formed from the reaction of SO₂ with
of the bands on the average band at 915 cm\(^{-1}\) do not shift noticeably upon evacuation and are consistent with those obtained of a higher vibrational mode (1000 cm\(^{-1}\)) which is broadened due to the presence of SO\(_2\); this band was also present in the spectrum in the presence of dibenzofuran. All of the bands were reproducible with repeated vapor exposure at 10\(^{-6}\) Torr for 18 hr (Fig. 1b). We were also able to observe cycling of the intensities of these bands upon vapor exposure for up to three cycles; eg. 18 hr evacuation in vacuum on occasion selected the SO\(_2\). However, upon lengthy exposure (72 hr) in high pressure (120 Torr) spectrum 1a resulted which could not be removed by lengthy evacuation. The bands at 908, 1002, and 1073 cm\(^{-1}\) for the complex which correspond to the SO\(_2\) band and obviously correspond to two stretching vibrational modes the fact that three such bands were present indicates that more than one type of complex is probably being detected. The analogous bands on bands at 612- and 214 cm\(^{-1}\) shifted little upon evacuation. The similar bands could correspond to the ν=0-mode. The bands at 815, 925, 1035, and 1180 cm\(^{-1}\) did not shift appreciably upon exposure. Peaks at 908 cm\(^{-1}\) have been assigned to the ν=1-mode. Interestingly with SO\(_2\), band positions for SO\(_2\) complex species are shown in parenthesis. Again reversibility was observed on long exposure time and pressure were minimized. It is clear that at least two types of Na[Al\(_2\)SO\(_4\)]/SO\(_2\) complexes were formed in these experiments - one in which the SO\(_2\) bands reversible and one in which the SO\(_2\) is coordinated in an irreversible fashion. Comparison of the intensities of the 903, 910, and 970 cm\(^{-1}\) bands in spectra 1a and 2c reveals that the reversible complex can decompose to the irreversible one even during evacuation following high SO\(_2\) exposures.
Both samples of the two final hexamethyl bridged complexes were prepared for the infrared in a KBr matrix containing enough of the sample to make

a spectrum. Condition for the sample film, the infrared analysis of the two
dithiocarbamate complexes indicated that the bridging bond for each
type of bond was the same. The data taken with the spectrometer at 600
infrared bands in the 800-1600 cm\(^{-1}\) region of the spectra imply that the
two forms of each complex contain 100% bonded in a bridging mode, with more
than 90% of the 13C-C ratio involved in the bridge. Final structure determination
must await 2-D ray structural data.

It should be noted that Madelkof and coworkers have reported recently
the reaction of 100% several tetracyanobenzene in solution solution and in
toluene solution. They report a stabilization of HgL\(_2\)2HgL for their
solution studies, and they were not able to observe a solution.
Furthermore, they report an infrared infrared band in the 1500-1600 cm\(^{-1}\)
region which are not observed for the HgL\(_2\)2HgL complex film. However,
their experimental conditions (liquid phase, 760 Torr 96% moisture for 48
hr) were vastly different than those used in this work, thus it is
possible that a reversible complex was formed also in their work, but
converted to an irreversible product before analysis.

Acknowledgment

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Corporation, and the Auburn University Energy Grant-in-Aid program for
partial support of this work. They also thank C.A. Madelkof for a preprint
of reference 7.


(5) Anal. Calcd (Atlantic Microlabs, Inc.) for Mn(PPHMe2)Br2·1/2H2O:
C 25.0, H 2.9, Br 41.5, S 4.2. Found: C 24.8, H 3.0, Br 41.4,
S 4.1; Anal. Calcd (Atlantic Microlabs, Inc.) for Mn(PF3)Br2·1/2H2O:


(7) McDuffie, C. A.; Barratt, D. E.; Benson, G. G.; Yannon, S. F.
Figure Captions

Figure 1. The infrared spectra of a Mn(PPhMe$_2$)Br$_2$ film:
(a) following initial preparation; (b) following exposure to 50 Torr SO$_2$ for 24 hr at 298 K and then brief evacuation; (c) following an evacuation cycle for 12 hr at 10$^{-6}$ Torr at 298 K; (d) following exposure to 120 Torr SO$_2$ for 72 hr at 298 K and lengthy evacuation.

Figure 2. The infrared spectra of a Mn(PEt$_3$)Br$_2$ film: (a) following initial preparation; (b) following exposure to 15 Torr SO$_2$ for 15 min at 298 K and then brief evacuation; (c) following an evacuation cycle for 24 hr at 10$^{-6}$ Torr at 298 K; (d) following exposure to 50 Torr SO$_2$ for 24 hr at 298 K and then brief evacuation; (e) following evacuation for 24 hr at 10$^{-6}$ Torr at 298 K. Band positions for analogous $^{18}$O$_2$ complex spectra are given in parentheses.
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The interactions of the complexes Mn(PPhMe₃)Br₂ and Mn(PEt₃)Br₂ as films with SO₂ and S²- have been investigated using infrared spectroscopy as an analytical probe. It is clear from these preliminary studies that two types of complexes with SO₂ have been formed. When the MnLBr₂ films were exposed to low pressures of SO₂ for relatively short times, an MnLBr₂/SO₂ complex formed reversibly in that the SO₂ could be removed by prolonged evacuation. On the other hand, lengthy exposure of the MnLBr₂ films to higher pressures of SO₂ caused the irreversible formation of a complex having stoichiometry MnLBr₂·1/2SO₂. It is probable that the SO₂ bonds in some type of bridging fashion in both of the types of MnLBr₂/SO₂ complexes.

Infrared Spectroscopy, Manganese Complexes, Sulfur Dioxide

The title of the study is "The Interaction of Complexes Mn(PPhMe₃)Br₂ and Mn(PEt₃)Br₂ with Sulfur Dioxide."
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