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The Interaction of Complexes of Composition

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## ABSTRACT

The complexes MnBr$_2$PMe$_3$, MnBr$_2$PEt$_3$, and MnBr$_2$PPhMe$_2$ have been prepared as films on infrared windows under completely anhydrous conditions with care being taken to eliminate all free phosphine. These films have been exposed to *d*ioxygenation/evacuation cycles in a specially designed infrared cell with infrared spectra being monitored under carefully controlled conditions. This work has indicated that such complexes do exist in solid-state films and do interact with dioxygen. However, the extent of the reversibility of the interaction with dioxygen is markedly dependent upon the nature of the tertiary phosphine ligand employed. All of the solid-state complexes studied in this work exhibit an irreversible decay channel in the presence of dioxygen to a phosphine oxide complex decomposition product at ambient temperature.

## INTRODUCTION

There exists a lively controversy at the present time concerning the existence of complexes of composition $MnLX_2$ (L = tertiary phosphine, X = anion) and their interaction 'th dioxygen. McAuliffe and coworkers first reported the preparation and characterization of a broad series of the manganese (II) complexes and suggested that the complexes mimicked myoglobin in their behavior with dioxygen.[1] Green and coworkers have subsequently cast doubt on the work of McAuliffe; they were not able to prepare complexes of composition $MnLX_2$ which reversibly interacted with dioxygen.[2] In fact they suggested that the dramatic color changes attributed by McAuliffe to $MnLX_2$ complexes reacting with dioxygen to form $MnLX_2 \cdot O_2$ complexes were due to a transient Mn (III) species formed in an $MnX_2/L$ system which ultimately decomposed by oxidizing the tertiary phosphine present.[2] McAuliffe has rebutted the arguments of Green and coworkers by emphasizing the need for preparing the $MnLX_2$ complexes under "absolutely anhydrous conditions" and by ensuring that excess phosphine is not present during the dioxygen uptake experiments.[3] Recently, crystal structures of similar $MnLX_2$ complexes[4] and of $Mn(PPhMe_2)I_2$[5] have been reported. In these laboratories considerable effort has been expended during the past three years in an attempt to answer some of the questions raised concerning the existence of the $MnLX_2$ complexes and the nature of the interaction of the complexes, if they do exist, with dioxygen. The primary analytical probe used in these studies has been infrared spectroscopy.

Our first attempt at preparing the $MnLX_2$ complexes for infrared

analyses generally followed the procedures reported by McAuliffe.[1] We were able to produce complexes which did uptake dioxygen accompanied by marked color changes, which did lose their color upon evacuation, which did exhibit these color changes upon several cycles of oxygenation/evacuation at room temperature, and which did provide elemental analyses in reasonable accord with the formula $MnLX_2$. However, all attempts to prepare pellets for infrared analysis under inert, anhydrous conditions provided samples which exhibited infrared bands near 3500–3450, 1600, and 550 $cm^{-1}$ indicative of moisture contamination. These samples did uptake dioxygen (not quantitative) and change color reversibly, but any cycling of infrared band intensities upon oxygenation/deoxygenation cycles seemed to be related to the intensities of the "water bands" such that definitive conclusions could not be advanced. Also, it was apparent that all infrared samples prepared in this manner were slowly decomposing to phosphine oxide and/or an $MnL'X_2$ (L' = phosphine oxide) complex because intense infrared bands at ca. 1150 $cm^{-1}$ grew with time . Ultimately the phosphine oxide complexes were not active in dioxygen uptake and did not undergo color change. Recently McAuliffe and coworkers have reported a similar decomposition process for the complexes in solution when in the presence of high pressure dioxygen and/or ambient temperature; however, they report numerous reversible cycles of dioxygen uptake and release at low temperature and pressure.[6]

A new technique for preparing the complexes for infrared analysis has been developed here recently which ensures that the complexes are free of moisture and excess phosphine contamination. In this procedure $MnX_2$ is carefully sublimed or sprayed as a THF or alcohol slurry onto a KBr

infrared window. The film of $MnX_2$ produced is then heated under evacuation in an infrared cell to liberate all water. The dry film is exposed to dry tertiary phosphine vapor generally at room temperature through the vacuum system which produces an anhydrous $MnLX_2$ film. Lengthy evacuation (ca. $10^{-6}$ torr) is employed to remove all traces of excess phosphine. The sample can then be subjected to dry dioxygen/evacuation cycles, and infrared analysis can be performed with no chance of moisture contamination. A preliminary communication describing the infrared analyses of $MnBr_2PMe_3$ and $MnBr_2PMe_3 \cdot O_2$ films has appeared recently.[7] The purposes of this paper are to describe our studies of $MnBr_2PMe_3$ in more detail and to present recent data concerning the complexes $MnBr_2PEt_3$ and $MnBr_2PPhMe_2$.

## EXPERIMENTAL SECTION

Manganese (II) bromide (Cerac, Inc.) which is preheated to 673 K under vacuum for 6 h and handled in a dry box is sublimed onto a KBr infrared window mounted in a sublimator designed in these laboratories. This is accomplished by slowly raising the temperature of the sublimator over a 2 h period to ca. 823 K. This temperature is then maintained for a period of 30-90 min depending upon the thickness of $MnBr_2$ film desired. The KBr window containing the $MnBr_2$ film is then transferred in a dry box to one of several infrared cells designed in these laboratories ( eg. Figure 1). It should be noted that the $MnBr_2$ film can also be prepared by spraying a slurry of $MnBr_2$/THF or MeOH onto a heated KBr window (less than 373 K); evaporation of the solvent leaves the $MnBr_2$ film. The

spectroscopic properties of the $MnBr_2PMe_3$ complex prepared from the $MnBr_2$ deposited by either method are the same, indicating minimal structural change of $MnBr_2$ caused by sublimation.

The $MnBr_2$ film in the infrared cell is heated under vacuum to <u>ca.</u> 493 K at $10^{-6}$ torr for sufficient time (usually 5-12 h) to remove all water. When a continuous baseline in the infrared spectrum is obtained, the film is exposed through the grease-free vacuum system to a tertiary phosphine at its vapor pressure for 30 min ($PPhMe_2$), 2 h ($PEt_3$), or at 400 torr for 45 min ($PMe_3$). The phosphines (Strem Chemicals, Inc.) are distilled and subjected to repeated freeze/thaw evacuation cycles before use. The film containing $MnBr_2PR_3$ is then subjected to evacuation at $10^{-6}$ torr for 4-12 h at room temperature to remove all traces of excess phosphine. Following this treatment infrared spectra (Perkin-Elmer model 580 or model 983 with data station) are monitored before and after exposure to dioxygen ($^{16}O_2$, Mathesen UHP; $^{18}O_2$, Alfa), evacuation, etc.

**RESULTS AND DISCUSSION**

The Trimethylphosphine Complex of $MnBr_2$

The infrared spectra of films of $MnBr_2$, $MnBr_2PMe_3$, $MnBr_2PMe_3 \cdot O_2$, and $MnBr_2OPMe_3$ and of the ligands $PMe_3$ (gas) and $OPMe_3$ (solid film) were presented in an earlier communication.[7] The spectra for $PMe_3$ and an $MnBr_2$ film exposed to $PMe_3$ were substantially different in terms of band frequencies and relative band intensities indicating that a complex had formed. The same was true for the spectra of $OPMe_3$ as compared to a $MnBr_2$ film exposed to $OPMe_3$. To provide substantiating evidence for the

existence of the $MnBr_2PMe_3$ complex, the suspected complex film was exposed to dioxygen at a pressure of 400 torr and a temperature of 523 K for 2 h until all of the blue color disappeared, and the infrared spectrum became almost identical with that of the $MnBr_2/OPMe_3$ film. At this high temperature a band near 1150 $cm^{-1}$ for free $OPMe_3$ sublimed from the film was also observed. The stoichiometry of the phosphine oxide complex was determined by preparing a sample in a sealed tube under the same conditions; an elemental analysis of this sample showed the stoichiometry to be $MnBr_2OPMe_3$.[7,8] Recently in these laboratories it has been shown by infrared that an $MnCl_2/PMe_3$ film converts to $MnCl_2OPMe_3$ upon standing in the presence of dioxygen at a pressure of 100 torr at room temperature for ten days with no decomposition to free $OPMe_3$. These observations can only rationally be explained by the existence of the complex $MnX_2PMe_3$ upon exposure of $MnX_2$ to free $PMe_3$. Thus we do support the claims of McAuliffe concerning the existence of $MnX_2PR_3$ complexes, at least as regards solid-state films.

The earlier work in these laboratories[7] established that upon exposure of an $MnBr_2PMe_3$ film to $^{16}O_2$ at a pressure of 100 torr at room temperature for 5 h, new infrared bands at 1132, 1060, 865, 570, and 409 $cm^{-1}$ become evident (see Fig. 2 in ref. 7). All of these bands occur at lower frequency (1095, 1040, 860, 545, and 395 $cm^{-1}$) if an identical sample is exposed to $^{18}O_2$ indicating that at least one oxygen atom is involved in all of the vibrational modes represented. The bands at 865 and 409 $cm^{-1}$ initially are weak but grow in intensity with time of exposure to dioxygen and are present (862, 400 $cm^{-1}$) also in the spectrum of the authentic $MnBr_2OPMe_3$ complex, so it can be assumed that these bands

may be assigned to the oxide complex which is the final decomposition product. An intense band near 1130 $cm^{-1}$ also occurs for the phosphine oxide complex. However, we believe that the initial band at 1132 $cm^{-1}$ which is evident for the film during the initial stages of dioxygenation while it is dark blue must refer at least in part to a vibrational mode for the oxygenated complex $MnBr_2PMe_3 \cdot O_2$. This band decayed in intensity and broadened concomitantly with the band at 570 $cm^{-1}$ upon increased exposure time to dioxygen. Finally when the color of the film disappeared, the 570 $cm^{-1}$ band vanished, and the 1132 $cm^{-1}$ band became very broad and weak. A band at 1130 $cm^{-1}$ grows in again as the final phosphine oxide decomposition product (white) is formed as the predominant species. For dioxygen complexes, an infrared band in the 1100–1200 $cm^{-1}$ region is indicative of an O-O stretching mode for a dioxygen species bonded in an end-on, bent configuration.[9-13] We believe that the dioxygen is present as a superoxide species with Mn in the III oxidation state providing the chromophore. This postulate is in accord with one of the conclusions of Green and coworkers, but it should be emphasized that we are considering specifically the solid-state $MnBr_2PMe_3$ film. It is possible that other oxygenated $MnX_2PR_3$ complexes and $MnX_2PR_3$ complexes in solution in general may not involve a superoxide species or that the oxygenated complexes of McAuliffe prepared differently from ours may have different structures. It should be noted that a superoxide manganese phthalocyanine dioxygen adduct has also been reported recently.[13] The 570 $cm^{-1}$ band for $MnBr_2PMe_3 \cdot O_2$, which is broad and has rather low intensity, could then be assigned to the Mn-O stretching mode in the transient superoxide species.

The $1060$ cm$^{-1}$ band for the MnBr$_2$PMe$_3 \cdot$O$_2$ complex grows steadily with exposure time to dioxygen but does not vanish when the complex finally loses its blue color. Ultimately the $1060$ cm$^{-1}$ band does decline in intensity with a concomitant growth of the oxide band at $1130$ cm$^{-1}$. This indicates that a second transient intermediate is being formed along the decomposition reaction pathway to MnBr$_2$OPMe$_3$. Work in these laboratories concerning the reaction of gas-phase PMe$_3$ and O$_2$ has shown that a similar infrared band near $1060$ cm$^{-1}$, which is not present in the infrared spectrum for OPMe$_3$, occurs.[14] For the gas-phase reaction this band can be assigned to PMe$_2$OMe (the infrared spectrum of PMe$_2$OMe contains a strong band at $1068$ cm$^{-1}$).[15] Thus we attribute the band at $1060$ cm$^{-1}$ for the MnBr$_2$PMe$_3 \cdot$O$_2$ complex to an alkoxyphosphine complex which subsequently isomerizes to the phosphine oxide final decomposition product. This process occurs slowly for the complex at room temperature, but can be expedited by heating in the presence of dioxygen (400 torr) at 583 K for 13 h. It should be noted that heating a MnBr$_2$PMe$_3 \cdot$O$_2$ film in the presence of dioxygen causes the formation of a new infrared band at $1040$ cm$^{-1}$ as well as the feature at $1130$ cm$^{-1}$. The final MnBr$_2$OPMe$_3$ complex does not exhibit this band at $1040$ cm$^{-1}$, so presumably it signifies another decomposition intermediate, possibly a dialkoxyphosphine complex or a MnBr$_2$OPMe$_2$OMe complex (the infrared spectrum of free OPMe$_2$OMe gives a prominent band at $1044$ cm$^{-1}$).[16]

Another controversial point concerning MnBr$_2$PR$_3$ interaction with dioxygen is whether or not the interaction process is reversible. For the case of the MnBr$_2$PMe$_3$ film we can see little evidence of a reversible interaction. Extensive evacuation at room temperature does not cause

significant decline of the superoxide infrared bands nor loss of the intense blue color. When the color finally does disappear upon heating or in the presence of high pressures of dioxygen, the $MnBr_2PMe_3 \cdot O_2$ film has been converted into decomposition products (alkoxyphosphine and phosphine oxide complexes). We have not studied the behavior of the $MnBr_2PMe_3$ complex in solution or at low temperature and pressure.

It should be noted that McAuliffe and coworkers have recently questioned our early work concerning the interaction of $MnBr_2PMe_3$ with dioxygen and the subsequent decomposition of the superoxide species to the $MnBr_2OPMe_3$ complex.[17] They exposed a sample of solid-state $MnI_2PMe_3$ to dioxygen and vacuum sublimed the resulting dark green solid onto a cold finger leaving a "flesh-colored residue which contained Mn and I, but no C or P". An X-ray crystal structure was performed on the "dark green" crystals from the cold finger which revealed the material to be $MnI_3(PMe_3)_2$ and led the authors to suggest that $MnBr_2PMe_3 \cdot O_2$ and $MnBr_2OPMe_3$ are not formed in the oxygenation of $MnBr_2PMe_3$. To test this conclusion, we have recently exposed anhydrous $MnBr_2$ to $PMe_3$ in our vacuum sublimator, evacuated excess phosphine for 6 h, and exposed the resulting solid material to dry dioxygen at 150 Torr for 30 min and then 300 Torr for 30 min at ambient temperatures. Following subsequent evacuation, the resulting purple/blue solid was vacuum sublimed onto a KBr infrared window; this sublimation was accomplished in the range 623-633 K, and the crystals produced in the sublimate were white. The infrared window was transferred to an IR cell in a dry box. The resulting infrared spectrum contained the usual prominent bands at ca. 1125, 1080, and 1055 $cm^{-1}$ characteristic of oxygenated $MnBr_2PMe_3$ in an advanced state of

decomposition (to $MnBr_2OPMe_3$ and its inactive precursor - see next paragraph). We have produced essentially the same results using $MnI_2PMe_3\cdot O_2$ at a lower sublimation temperature (548 K). Thus it would appear that the $MnBr_2PMe_3\cdot O_2$ complex was produced as a film in these laboratories and that care should be exercised when attempting to sublime oxygenated complexes to minimize decomposition.

A speculative reaction scheme which is consistent with the facts which have been accumulated for the $MnBr_2PMe_3$ complex is shown in Figure 2. An X-ray crystal structure of the complex $MnI_2PPhMe_2$ has been determined by King and collaborators.[5] This structure shows the solid-state complex to be a polymeric array containing bridged halogens and manganese atoms alternating in tetrahedral/octahedral coordination. Two phosphine moieties are bonded to each octahedral manganese atom. Since there is no crystal structure available for any of the complexes studied in this work, we have chosen to use the King structure as a basis for our proposed speculative reaction scheme for $MnBr_2PMe_3$ in Figure 2. Our infrared evidence indicates that a transient superoxide species forms first; it is reasonable to assume that the dioxygen moiety would be bonded end-on to a tetrahedral manganese site. Decomposition could proceed by insertion of the two oxygen atoms into P-C bonds, possibly for phosphine moieties in different layers as indicated in the figure, to form an alkoxy phosphine complex. The process could then be repeated to form a complex having two alkoxy phosphine moieties. Finally, isomerization would give the final phosphine oxide complex having the correct stoichiometry. Of course, other speculative reaction schemes could be written which might rationalize the data. For example, the dioxygen could break a MnBr bridge

and bind to an octahedral Mn containing the two phosphine ligands.[18]  Then the superoxide could decompose to a complex having two alkoxy phosphine moieties followed by isomerization to the final phosphine oxide complex.

## The Triethylphosphine Complex Of MnBr$_2$

The behavior of the MnBr$_2$PEt$_3$ complex upon interaction with dioxygen is quite different from that of the MnBr$_2$PMe$_3$ complex.  For example, for the MnBr$_2$PEt$_3$ complex film we have been able to achieve several cycles of exposure to dioxygen followed by evacuation during which the color changes from dark blue to a very faint blue or white color indicating possible reversible interaction of the complex with the dioxygen.  This process is much slower for the solid-state films than it is for solutions and is accompanied by continual decomposition to the MnBr$_2$OPEt$_3$ complex at ambient temperature.  The infrared spectra corresponding to a series of such cycles are shown in Figure 3.

Figure 3a represents the infrared spectrum of a film of MnBr$_2$PEt$_3$ prepared in the manner discussed earlier.  This spectrum is quite different than that of gas-phase PEt$_3$ indicating that reaction of MnBr$_2$ and the phosphine has occurred.  Following exposure of the film to $^{16}O_2$, spectrum 3b was recorded.  One notes that the only significant spectral developments are a new band at 1130 cm$^{-1}$ and a greatly accentuated band at 1030 cm$^{-1}$.  Upon exposure of another MnBr$_2$PEt$_3$ film to $^{18}O_2$ (spectrum 3b′), the 1130 cm$^{-1}$ band shifts to 1095 cm$^{-1}$, and a weak new feature is noted at 615 cm$^{-1}$.  The 1030 cm$^{-1}$ band again is accentuated but does not shift to lower wavenumber.  We believe that the 1130/1095 cm$^{-1}$ band most

probably again corresponds to an O–O stretching mode for a superoxide linkage. The 615 cm$^{-1}$ band was very weak, but may correspond to an Mn–O vibrational mode for the superoxide species. This band was not evident for spectrum 3b, but it could lie under the spectral features near 650 cm$^{-1}$. The corresponding band for MnBr$_2$PMe$_3$ occurred at 570/545 cm$^{-1}$; it is not clear why the band should lie at significantly higher wavenumber for the PEt$_3$ complex.

The 1030 cm$^{-1}$ band cycles in intensity upon dioxygenation/evacuation cycles (see Figure 3a, b, c, d). However, the band does not shift to lower wavenumber upon exposure to $^{18}$O$_2$ (see Figure 3b′). This indicates that the band must correspond to a ligand vibrational mode. The fact that the band cycles in intensity upon dioxygenation/evacuation is reasonable evidence for a reversible interaction of dioxygen with the MnBr$_2$PEt$_3$ complex film. However, it should be noted that the band at 1130 cm$^{-1}$ actually grows in intensity upon evacuation (Figure 3c). Thus while the complex reversibly interacts with dioxygen, it must exhibit a competing irreversible decomposition step to the phosphine oxide complex which fortuitously has a P–OPEt$_3$ vibrational mode near 1130 cm$^{-1}$. After the complex loses its color upon extensive contact with dioxygen, a large infrared band with its maximum at 1110 cm$^{-1}$ (Figure 3e) is observed.

In summary, the MnBr$_2$PEt$_3$ complex seems to interact reversibly with dioxygen, whereas the MnBr$_2$PMe$_3$ does not appreciably. However, the MnBr$_2$PEt$_3$ also decomposes much more rapidly in dioxygen than does MnBr$_2$PMe$_3$ at ambient temperature. Whether the behavior of the MnBr$_2$PEt$_3$ complex in the presence of dioxygen can be explained by the reaction scheme in Figure 2 is not clear from this study. The band noted for a

$MnBr_2POMeMe_2$ complex at $1060$ cm$^{-1}$ which should shift when $^{18}O_2$ is employed is not evident in any of the spectra shown in Figure 3. Of course, it could lie under the extensive band system at $1080-1000$ cm$^{-1}$, such that its behavior could not be monitored.

## The Phenyldimethylphosphine Complex Of $MnBr_2$

The behavior of the $MnBr_2PPhMe_2$ complex in the presence of dioxygen is quite different from that of the two trialkyl complexes. We have observed several cycles of dioxygenation/evacuation by observation of color changes of the film; however, there are no infrared bands which cycle in intensity for this complex.

Figure 4 shows the infrared spectra of $PPhMe_2$ and an $MnBr_2$ film exposed to $PPhMe_2$. It is evident that significant changes in band intensities and wavenumbers have occurred supporting our contention that an $MnBr_2PPhMe_2$ film has been produced.

Figure 5 illustrates the behavior of the $MnBr_2PPhMe_2$ complex upon exposure to $^{16}O_2$ and subsequent evacuation as evidenced by sequential infrared spectra. In Figure 5a a weak band occurs at $1109$ cm$^{-1}$ which can probably be attributed to the P-C stretching vibrational mode for the phosphorus-phenyl linkage. The intensity of this band is accentuated upon exposure to dioxygen (Figure 5b). New bands also appear at $1148$ and $435$ cm$^{-1}$ following exposure to dioxygen (Figure 5b), but these bands continue to develop even following evacuation (Figure 5c) and remain intense after the complex has lost its activity (Figure 5e). There is little doubt that these two bands may be assigned to the $MnBr_2OPPhMe_2$ decomposition product

because Figure 5e is almost identical to the infrared spectrum of an authentic $MnBr_2OPPhMe_2$ film prepared by exposing $MnBr_2$ to $OPPhMe_2$ (Figure 6). Any band due to the dioxygen adduct $MnBr_2PPhMe_2 \cdot O_2$ (Figure 5b) must be masked by the intense phosphine oxide complex band at 1148 $cm^{-1}$. Furthermore, there was no new band detected in the 500-650 $cm^{-1}$ region for the oxygenated complex, although a broad, weak band could easily be masked by the ligand band near 700 $cm^{-1}$ which has a broad low-energy shoulder (Figure 5a-e). The fact that the band at 1148 $cm^{-1}$ continues to grow during evacuation is evidence that under these reaction conditions a dioxygen adduct is rapidly decomposing to the $MnBr_2OPPhMe_2$ decomposition product.

Figure 7 shows the infrared spectra of an $MnBr_2PPhMe_2$ film exposed to $^{18}O_2$. Upon brief exposure the 1109 $cm^{-1}$ ligand band shifts slightly to 1105 $cm^{-1}$, and two new bands are formed at 1132 and 1088 $cm^{-1}$. However, all of these bands remain for the final $MnBr_2^{18}OPPhMe_2$ decomposition product. Thus we must conclude that decomposition is rapid for $MnBr_2PPhMe_2$ in the presence of dioxygen. The only evidence for reversibility is the fact that the color disappears upon evacuation (Figure 5c) and reappears upon further exposure to dioxygen (Figure 5d). Of course, this observation could also be explained by incomplete reaction of $MnBr_2PPhMe_2$ (Figure 5b) with dioxygen before evacuation was initiated, such that some complex remained for reaction upon further exposure (Figure 5d). Thus although phenyldialkyl phosphine complexes of $MnBr_2$ have been postulated to interact rapidly and reversibly with dioxygen in solution,[4] in a solid-state film the $MnBr_2PPhMe_2$ complex decomposes rapidly in competition with evacuation of the complexed dioxygen. Whether the

reaction scheme proposed in Figure 2 is valid for this complex could not be determined in this work.

## CONCLUSIONS

The interaction of dioxygen with tertiary phosphine complexes of $MnBr_2$ for solid-state films is markedly dependent upon the nature of the tertiary phosphine ligand employed. The $MnBr_2PMe_3$ complex is quite stable toward decomposition to $MnBr_2OPMe_3$ upon exposure to dioxygen, but it also shows little tendency toward reversibility during dioxygenation/evacuation cycles. In fact the blue color can not be removed by prolonged evacuation, and it only disappears following decomposition. On the other hand, cycles of color/colorless can be obtained for $MnBr_2PEt_3$ and $MnBr_2PPhMe_2$ upon dioxygenation/evacuation, but these complexes decompose (especially $MnBr_2PPhMe_2$) competitively to the phosphine oxide complexes. The $MnBr_2PEt_3$ complex film was the only one in this study which exhibited an infrared band which clearly cycles in intensity upon dioxygenation/evacuation cycles. Finally, it should be noted that recent work here has demonstrated that the chloride analogs of the three complex films discussed in this work behave in similar fashion to the bromide complex films.[19]

## ACKNOWLEDGEMENTS

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**FIGURE CAPTIONS**

Figure 1.  A typical pyrex infrared cell employed in this work.

Figure 2.  Reaction scheme for the interaction of dioxygen with the $MnBr_2PMe_3$ complex (see text).

Figure 3.  Infrared spectra of $MnBr_2PEt_3$, $MnBr_2PEt_3 \cdot O_2$, and $MnBr_2OPEt_3$: (a) complex film prepared as described in the text;  (b) following exposure to 88 torr of $^{16}O_2$ for 60 min and then 246 torr of $^{16}O_2$ for 40 min;  (b´) a second complex film following exposure to 200 torr $^{18}O_2$ for 90 min;  (c) film from (b) evacuated at $\underline{ca.}$ $10^{-6}$ torr for 20 h at room temperature;  (d) further exposure of film from (c) to 280 torr $^{16}O_2$ for 90 min (blue), followed by evacuation for 18 h (white), followed by exposure to 230 torr $^{16}O_2$ for 4 h;  (e) further exposure of film from (d) to 550 torr $^{16}O_2$ for 24 h.

Figure 4.  Infrared spectra of a liquid film of $PPhMe_2$ on a KBr window and a film of $MnBr_2$ exposed to $PPhMe_2$ as discussed in the text.

Figure 5.  Infrared spectra of $MnBr_2PPhMe_2$, $MnBr_2PPhMe_2 \cdot {}^{16}O_2$, and $MnBr_2{}^{16}OPPhMe_2$: (a) complex film prepared as described in the text; (b) following exposure to 53 torr $^{16}O_2$ for 5 h; (c) following evacuation at $\underline{ca.}$ $10^{-6}$ torr for 48 h;  (d) following further exposure to 48 torr $^{16}O_2$ for 1 h;  (e) following further exposure to 48 torr $^{16}O_2$ for 24 h at room temperature.

Figure 6.  Infrared spectra of solid-state film of $OPPhMe_2$ and a film of $MnBr_2$ exposed to sublimed $OPPhMe_2$.

Figure 7.  Infrared spectra of $MnBr_2PPhMe_2$, $MnBr_2PPhMe_2 \cdot {}^{18}O_2$, and $MnBr_2 {}^{18}OPPhMe_2$:  (a) complex film prepared as described in the text; (b) following exposure to 180 torr ${}^{18}O_2$ for 30 min;  (c) following further exposure to 180 torr ${}^{18}O_2$ for 15 h;  (d) following heating at 308 K in 180 torr ${}^{18}O_2$ for an additional 72 h (subsequent evacuation caused no spectral or color changes).
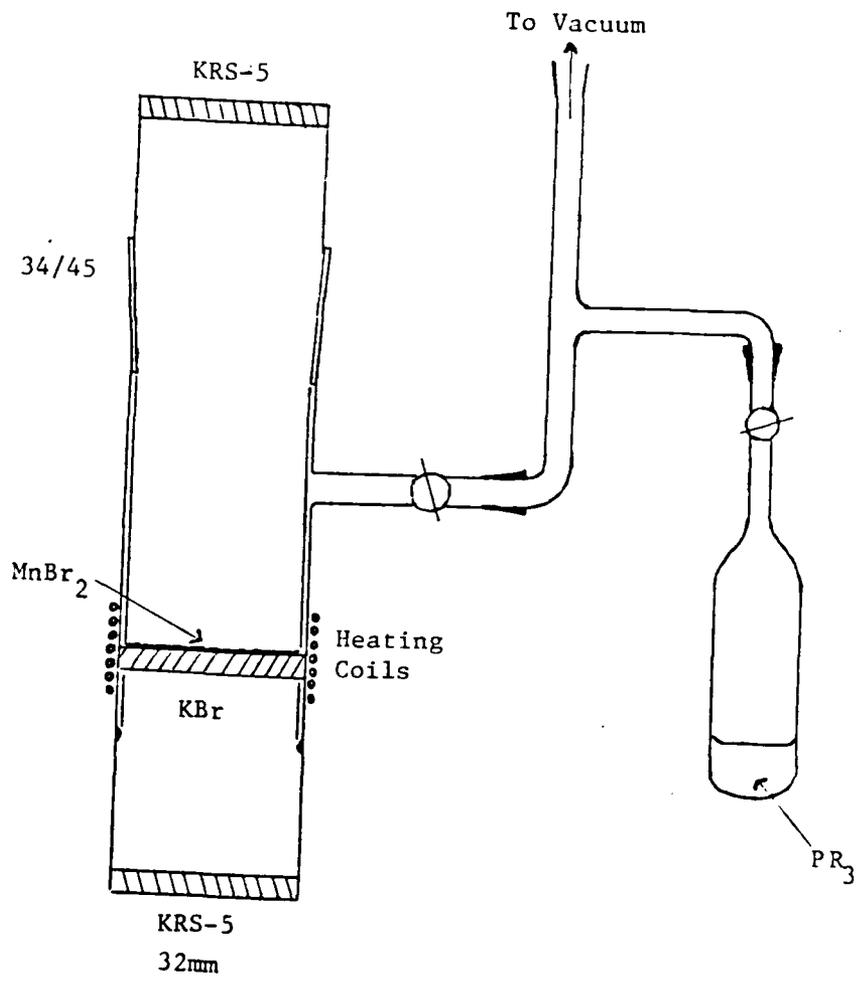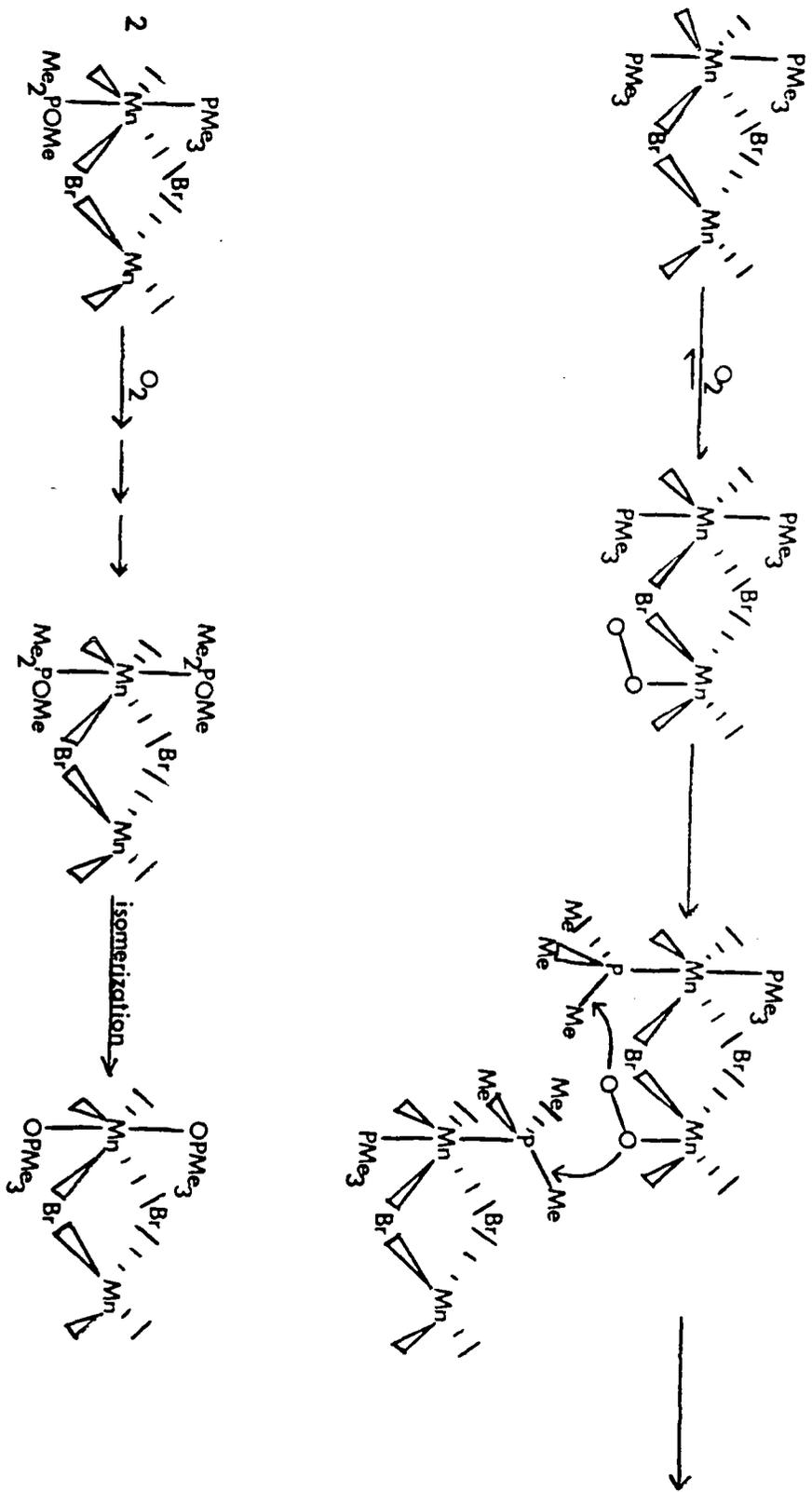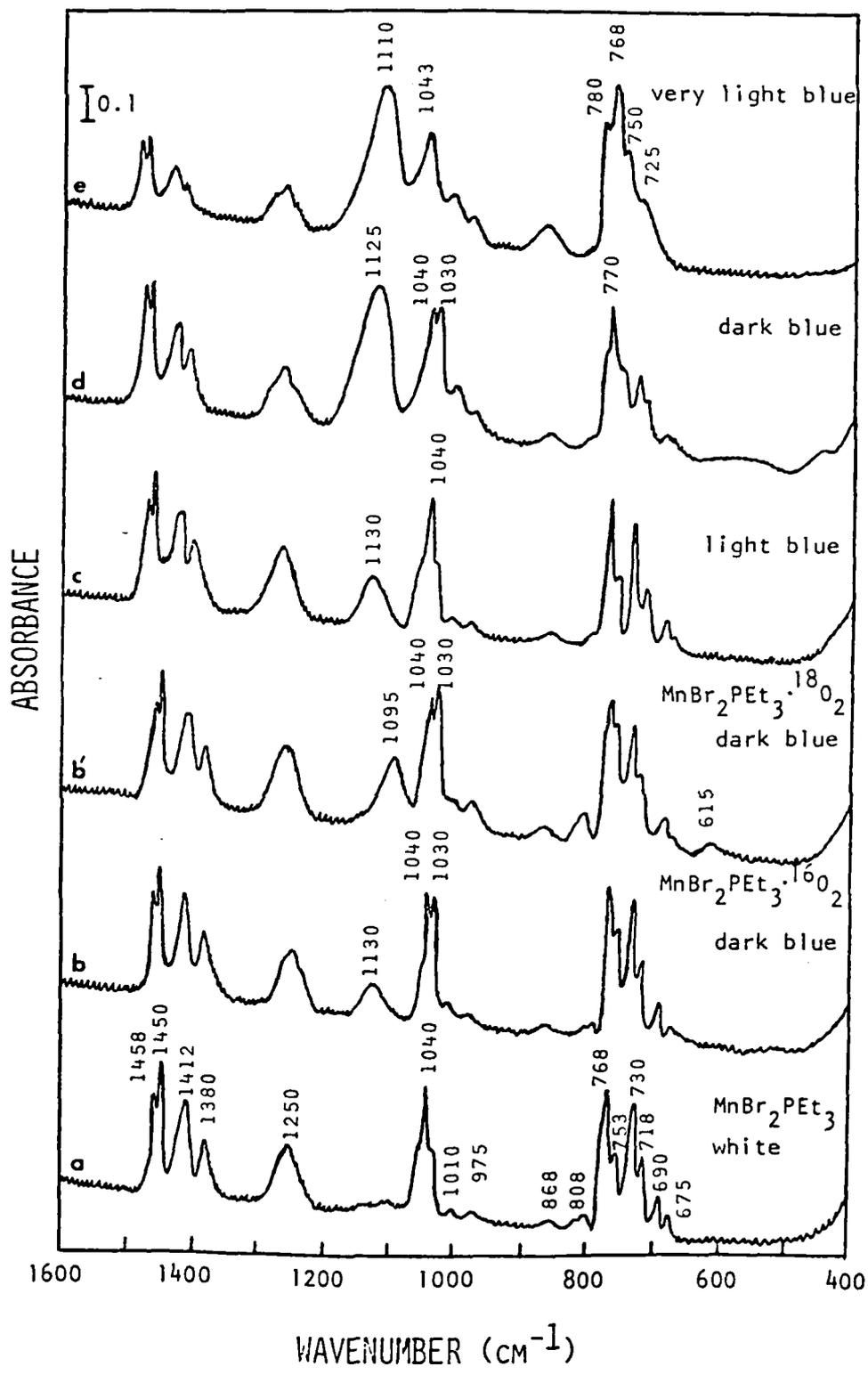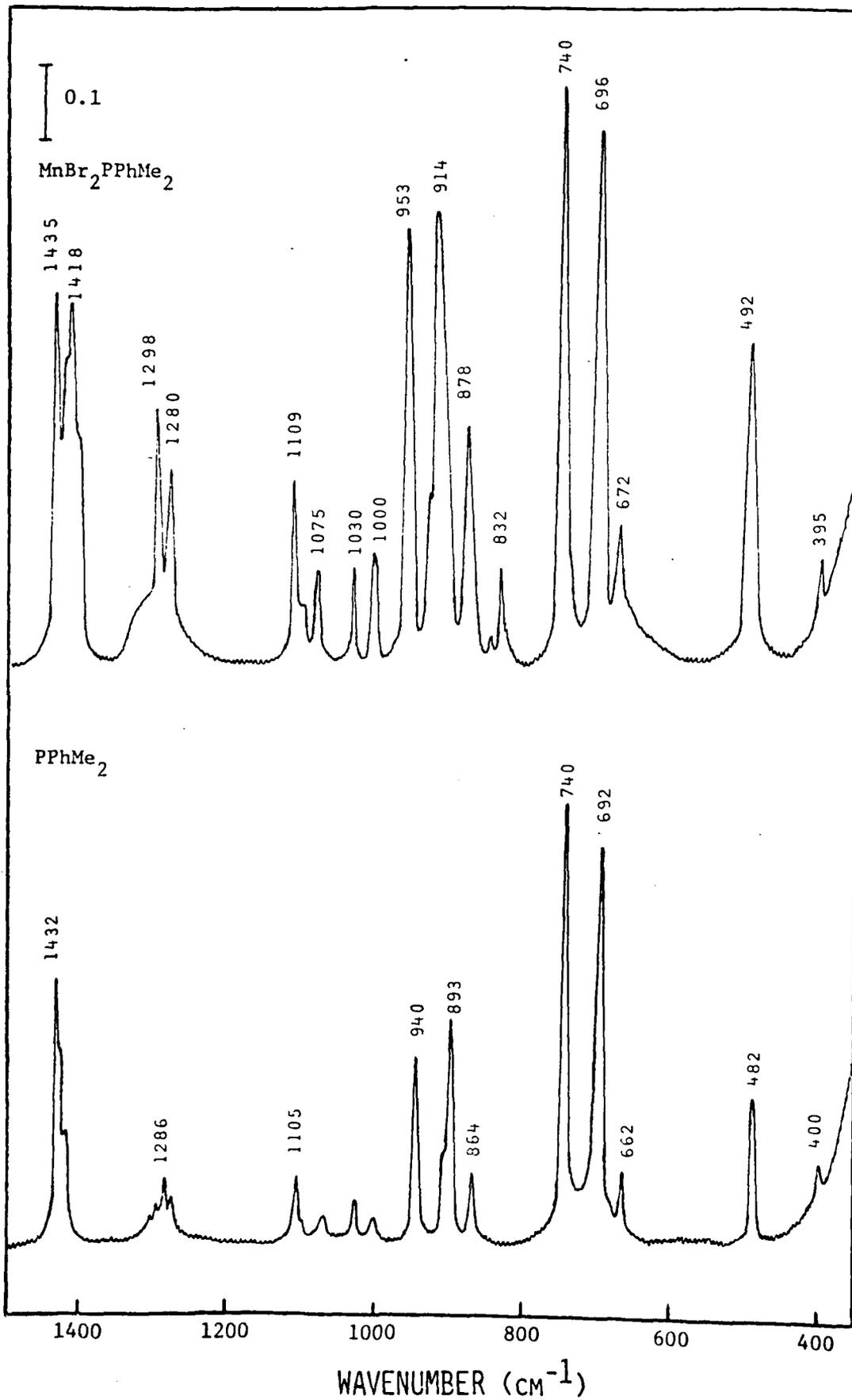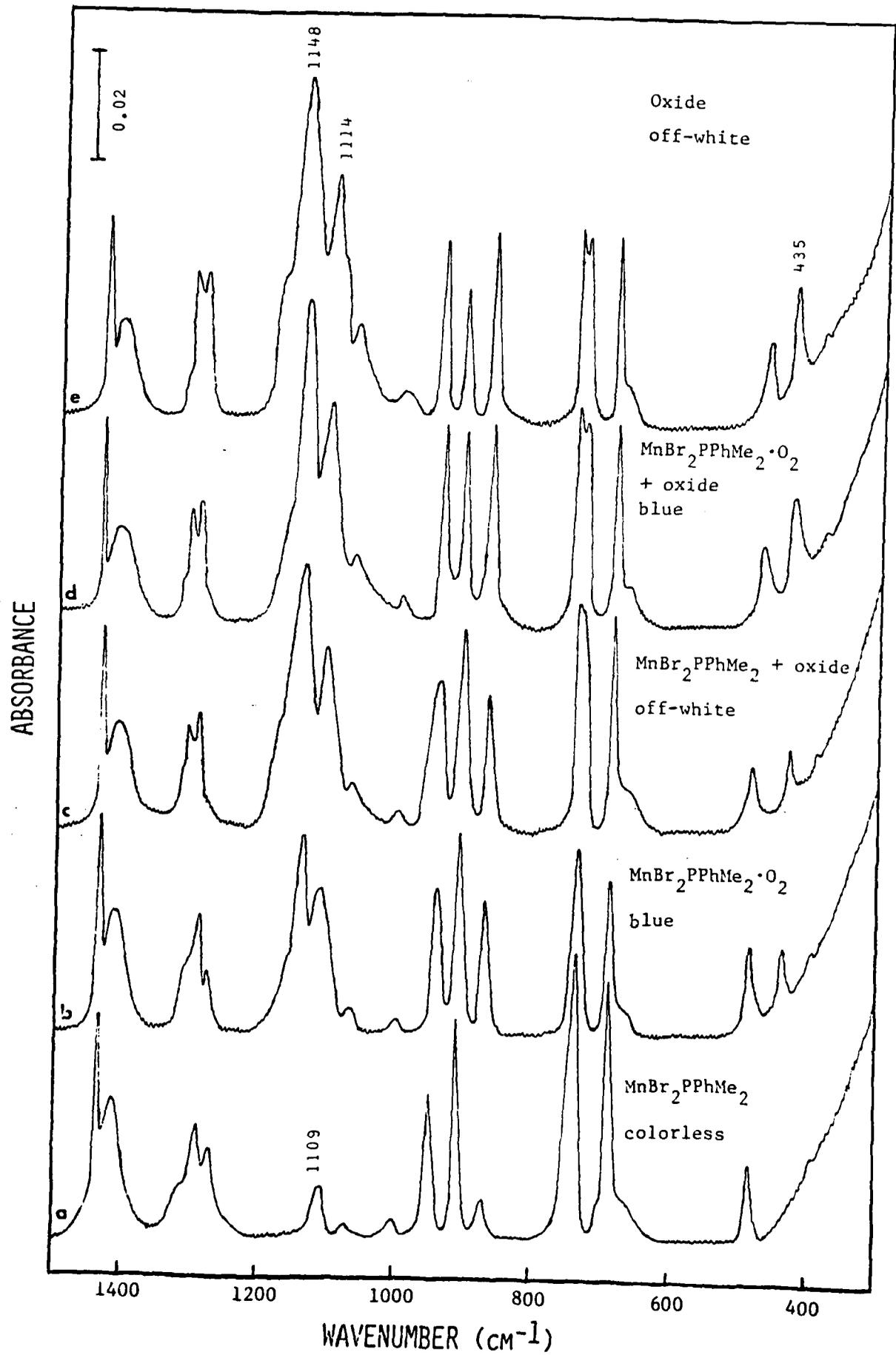
Fig 1

Fig.2

Fig.

Fig4

ABSORBANCE

0.02

1148

1114

Oxide
off-white

e

435

$MnBr_2PPhMe_2 \cdot O_2$
+ oxide
blue

d

$MnBr_2PPhMe_2$ + oxide

off-white

c

$MnBr_2PPhMe_2 \cdot O_2$

blue

b

1109

$MnBr_2PPhMe_2$

colorless

a

1400     1200     1000     800     600     400

WAVENUMBER ($CM^{-1}$)

Fig. 5

ABSORBANCE

OPPhMe₂

0.1

1436
1419
1324
1304
1290
1178
1122
942
908
869
743
727
699
491
433

MnBr₂OPPhMe₂

1438
1418
1302
1292
1148
1115
1070
939
908
868
748
732
694
489
438

WAVENUMBER(CM⁻¹)

1500   1300   1100   900   700   500   300

Fig

Oxide
off-white

$\mathbf{\bar{\boxed{}}}$ 0.05

d

$MnBr_2PPhMe_2 \cdot {}^{18}O_2$
15 hr, blue

c

$MnBr_2PPhMe_2 \cdot {}^{18}O_2$
30 min, blue

1132
1105
1048
1068

b

435

$MnBr_2PPhMe_2$

colorless

1109

a

ABSORBANCE

WAVENUMBER (cm$^{-1}$)

1400    1200    1000    800    600    400
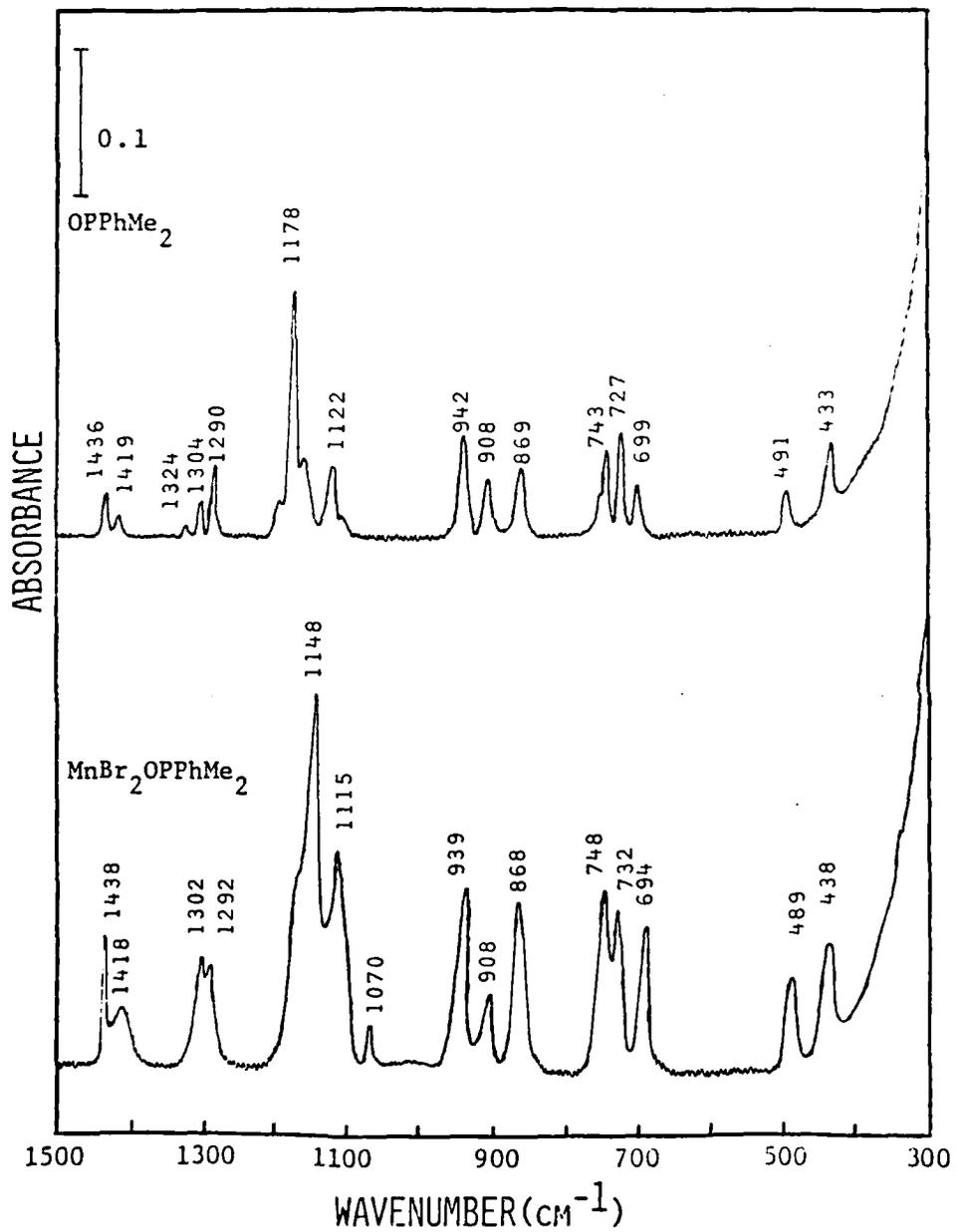
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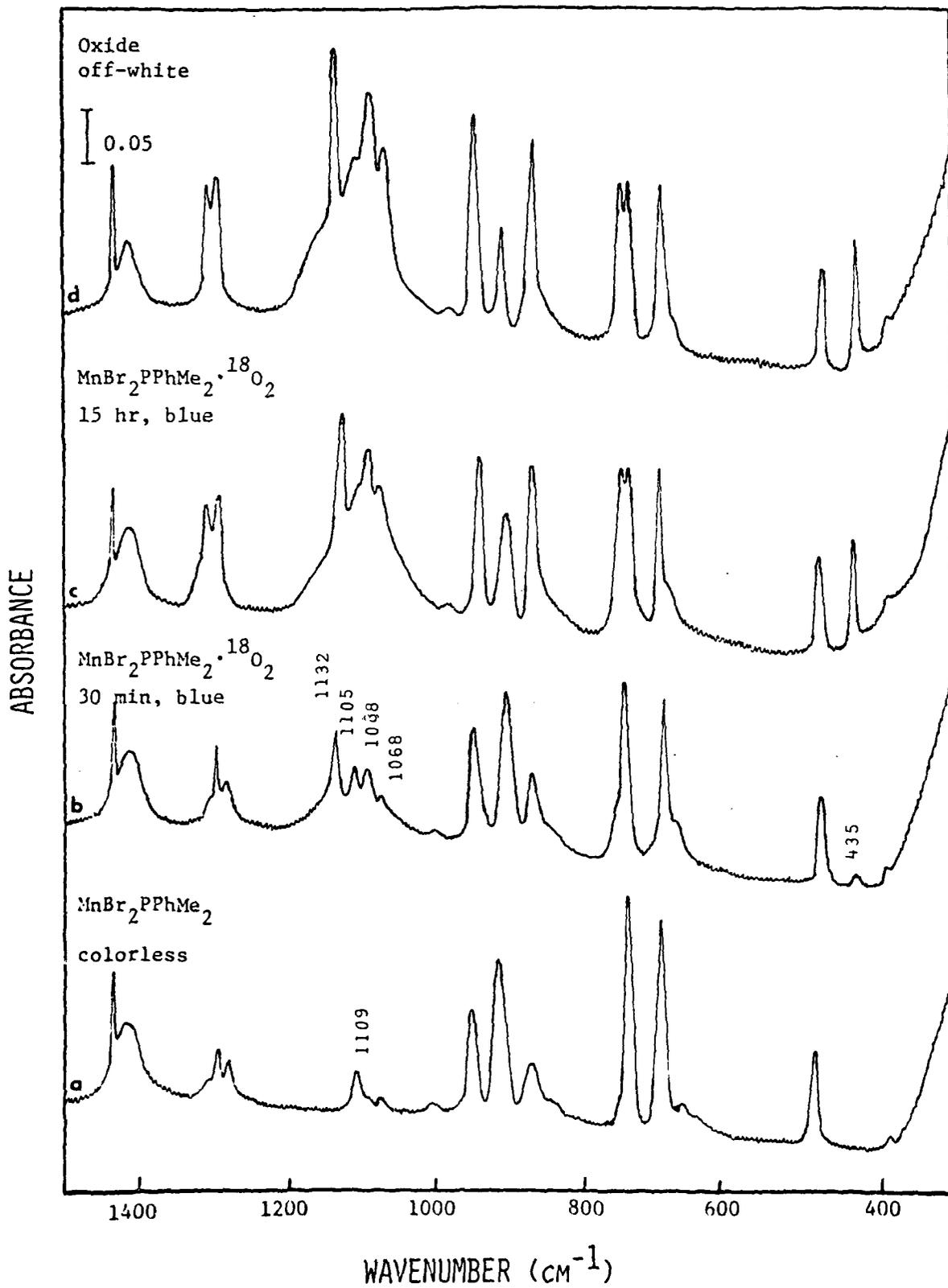
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