121175-68-6; $(\eta^3\text{-}C_3H_5)Mn(CO)_3^{\bullet-}$, 121175-69-7; $(OC)_5Cr^{\bullet-}$, 39586-86-2; $(OC)_4Fe^{\bullet-}$, 51222-96-9; $(OC)_3Ni^{\bullet-}$, 51222-94-7; CCl_4, 56-23-5; $CHCl_3$, 67-66-3; CH_2Cl_2, 75-09-2; CH_3Cl, 74-87-3; CCl_3CH_3, 71-55-6; CCl_2FCClF_2, 76-13-1; CCl_3F, 75-69-4; CCl_2F_2, 75-71-8; $CClF_3$, 75-72-9; CH_3Br, 74-83-9; CF_3Br, 75-63-8; CCl_3Br, 75-62-7; CH_3I, 74-88-4; CF_3I, 2314-97-8; $(OC)_4ReBrCl^-$, 121175-70-0; $(OC)_4ReBr_2^-$, 44965-51-7; $(OC)_4ReBrI^-$, 44965-52-8; $(OC)_4ReCl_2^-$, 78295-38-2; $(OC)_4ReClI^-$, 121175-71-1; $(OC)_4MnBrCl^-$, 44965-45-9; $(OC)_4MnBr_2^-$, 51153-35-6; $(OC)_4MnBrI^-$, 37176-06-0; $(OC)_3MnBrCl^-$, 121175-72-2; $(OC)_3MnBr_2^-$, 121175-73-3; $(OC)_3MnBrI^-$, 121175-74-4; $(OC)_4MnCl_2^-$, 52901-71-0; $(OC)_4MnClI^-$, 121175-75-5; $(OC)_3MnCl_2^-$, 121175-76-6; $(OC)_3MnClI^-$, 121175-77-7; $(\eta^3\text{-}C_3H_5)Re(CO)_3Cl^-$, 121175-78-8; $(\eta^3\text{-}C_3H_5)Re(CO)_3I^-$, 121175-79-9; $(\eta^3\text{-}C_3H_5)Re(CO)_2I^-$, 121175-80-2; $(OC)_5CrCl^-$, 14911-56-9; $(OC)_4CrCl^-$, 121175-81-3; $(OC)_5CrBr^-$, 14911-72-9; $(OC)_5CrI^-$, 14911-71-8; $(OC)_4FeCl^-$, 88083-34-5; $(OC)_4FeBr^-$, 88083-31-2; $(OC)_2Fe(Br)(CF_3)^{\bullet-}$, 88083-33-4; $(OC)_4FeI^-$, 44864-27-9; $(OC)_2Fe(I)(CF_3)^{\bullet-}$, 88105-33-3; $(OC)_3NiCl^-$, 44635-04-3; $(OC)_2NiCl^-$, 121175-82-4; $(OC)_3NiBr^-$, 44635-03-2; $(OC)_2NiBr^-$, 121175-83-5; $(OC)_3NiI^-$, 36830-71-4; $(OC)_2NiI^-$, 121175-84-6; $(OC)_3ReBrCl^-$, 121175-85-7; $(OC)_3ReBr_2^-$, 121175-86-8; $(OC)_3ReCl_2^-$, 121175-87-9.

Reversible Interaction of Dioxygen with $MnPEt_3Br_2$

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Abstract: The reversible interaction of dioxygen with a solid-state $MnPEt_3Br_2$ film at −30 °C has been observed. Infrared spectroscopic evidence and isotopic labeling studies have shown that the reversible dioxygen species formed is of the side-on peroxo variety. This work represents the first unambiguous spectroscopic observation of the reversible interaction of dioxygen with solid-state $MnPR_3X_2$ complexes.

Several years ago McAuliffe and co-workers reported the synthesis and properties of a series of manganese(II) complexes of composition $MnLX_2$ (L = tertiary phosphine, X = anion), which they suggested interacted reversibly with dioxygen.[1] Subsequent reports by Green et al.,[2] and from these laboratories,[3,4] showed that a reversible interaction of the complexes with dioxygen was indeed controversial. While the Green laboratory could find no evidence of such a reversible interaction for THF solutions of the alleged complexes,[2] we reported that the solid-state complex $MnPEt_3Br_2$ did exhibit a ligand infrared band at 1030 cm^{-1}, which cycled in intensity upon dioxygen exposure/removal cycles at ambient temperature.[4] However, we observed that the possible reversible dioxygen interaction was accompanied by a competitive irreversible decomposition process to the corresponding manganese phosphine oxide complex. We were not able to detect a dioxygen infrared band for the phosphine complex, which cycled in intensity upon exposure and removal of the dioxygen, although a band at 1130 cm^{-1} suggestive of a superoxo species was observed. Wickens and Abrams later reported the preparation and analyses of complexes having formulae $MnX_2(PMe_2Ph)$ (X = Cl, Br, I, or NCS), but although they observed dramatic color changes upon exposure to dioxygen, they could not detect reversibility within the constraints of their experiment.[5] The current work has spectroscopically identified unambiguously for the first time a reversible interaction of dioxygen with a $MnLX_2$ complex.

Experimental Section

We have found that during preparation of active solid-state films of $MnLX_2$ complexes water and air must be completely excluded from the reaction vessel; sample manipulation in an inert atmosphere in a drybox is not sufficient. In this work a new infrared cell reactor was designed that solved the problem. The cell (Figure 1), which was constructed from a 64-mm Pyrex tube, contained two external KRS-5 infrared windows along one axis held in place by Torr Seal vacuum epoxy and, on the axis perpendicular to that containing the IR windows, a quartz sublimation furnace and a port through which a volatile sample could be introduced. A third infrared window (KBr) was attached to a manipulator, which allowed rotation of the window into the infrared beam or facing the sublimator or volatile-sample-introduction port. The KBr window could be heated resistively by nichrome wire or cooled by chilled gas, e.g., liquid-nitrogen boiloff; its temperature was monitored by a chromel–alumel thermocouple. The cell could be evacuated to ca. 10^{-6} Torr by a cryopump/ion pump system.

The complex films used in this study were prepared as follows. Anhydrous $MnBr_2$ was placed in the quartz sublimator portion of the cell and was degassed under vacuum at 380 °C for 48 h; the KBr window was baked at 250 °C during the same time. Then $MnBr_2$ was sublimed onto the KBr window as a thin film by heating the salt at 550 °C for about 50 min at a pressure of 2×10^{-6} Torr. The film was then exposed to triethylphosphine at its vapor pressure for 10 min at room temperature to produce the complex $MnPEt_3Br_2$ as a film on the KBr window. Although it is not possible to directly verify that the film has the stated stoichiometry due to its sensitivity to dioxygen and moisture, previous work here based upon dramatic changes in the infrared spectrum of the film relative to that of free triethylphosphine and the formation of the phosphine oxide complex (analyzed as $MnOPEt_3Br_2$) upon decomposition of the complex after extensive exposure to dioxygen at ambient temperature provided compelling indirect evidence that the stoichiometry of the complex film is $MnPEt_3Br_2$.[4] Following evacuation of the excess and uncoordinated PEt_3 at room temperature for 165 min, the sample was cooled to −30 °C under evacuation, and an infrared spectrum was recorded (IBM 32/AT FTIR). Then the sample film was ready to be exposed to dioxygen.

The anhydrous $MnBr_2$ (Aldrich Chemical Co.) employed in this work had a stated purity of 99% and was used without further purification (except for the sublimation process in the cell reactor). Triethylphosphine (Strem Chemical Co.) was distilled onto 3A molecular sieves and subjected to freeze/thaw evacuation cycles before use. $^{16}O_2$ obtained from Matheson (99.99%) was further purified before use by passage through a molecular sieve trap at 195 K. $^{18}O_2$ (99.5%) was obtained from ICN Stable Isotopes and used without further purification.

Results and Discussion

A $MnPEt_3Br_2$ film prepared as described above was exposed to 56 Torr of $^{16}O_2$ at −30 °C (causing a dark red color), and the FTIR was monitored periodically over several hours. Although some of the ligand bands were affected by the interaction of the complex with dioxygen, the most notable change in the spectrum

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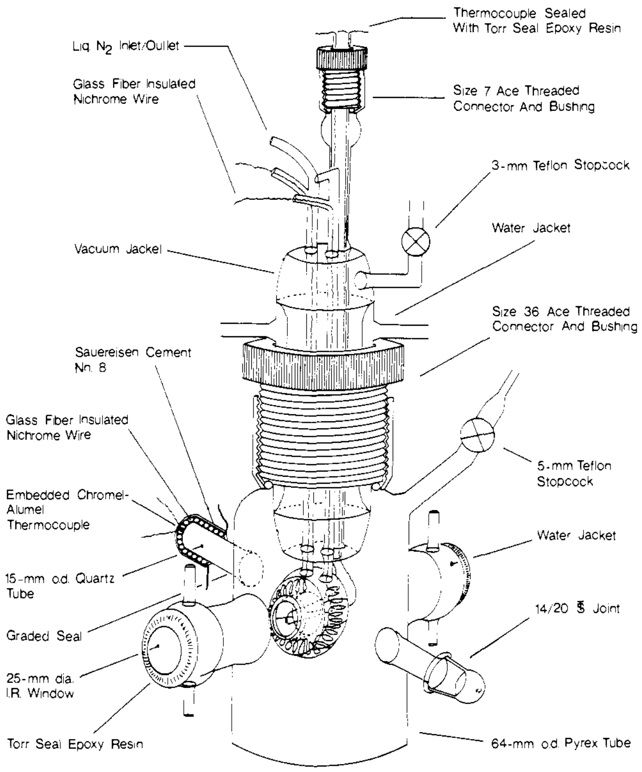

Figure 1. Variable-temperature infrared cell reactor.

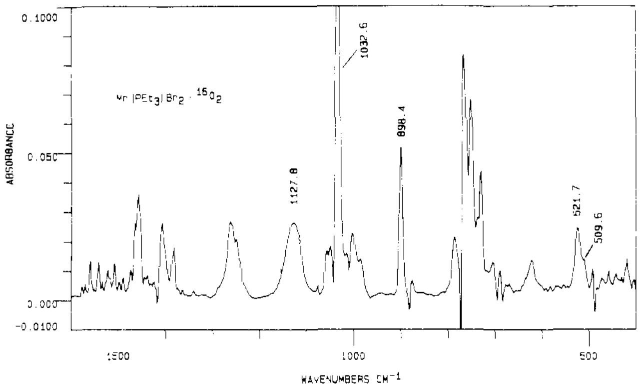

Figure 2. Infrared difference spectrum of the peroxo complex $MnPEt_3Br_2{}^{16}O_2$. A film of $MnPEt_3Br_2$ was exposed to 56 Torr of $^{16}O_2$ for 1.5 h at -30 °C.

was the appearance of strong new infrared bands at 898.4 and 521.7 cm^{-1}, with a shoulder at 509.6 cm^{-1} (Figure 2). These bands declined markedly in intensity upon evacuation, disappeared completely upon warming to ca. 10 °C, and reappeared upon further exposure to dioxygen at -30 °C. The sample film was blue when the bands were not present following evacuation. The bands at 1127.8 and 1032.6 cm^{-1} did not disappear upon evacuation and have been assigned previously to a mixture of a superoxo phosphine complex and a phosphine oxide decomposition product and to the PEt_3 ligand, respectively.[4]

Upon exposure of another $MnPEt_3Br_2$ film to 11 Torr of $^{18}O_2$ for 15 min, the same behavior was noted except the new infrared bands occurred at 850.5 and 498.3 cm^{-1} with a shoulder at 489.3 cm^{-1} (Figure 3). The isotopic shifts of 47.9 and 23.4/20.3 cm^{-1} are reasonably consistent with the expected shifts (harmonic oscillator approximation) of 51.4 and 23.1 cm^{-1} for an O–O stretch and an Mn–O stretch, respectively, for dioxygen coordinated to Mn. Furthermore, the band positions (and the presence of symmetric and antisymmetric components for the Mn–O moiety) are consistent with a peroxo dioxygen species bound side-on.[6-13] A much larger splitting of the symmetric and antisymmetric Mn–O modes would be expected for a bridged peroxo species (95 cm^{-1} for the peroxo-bridged complex $[(NH_3)_5CoOOCo(NH_3)_5](NO_3)_4$),[14,15] and if the peroxo-bridged species were centrosymmetric, only the antisymmetric Mn–O mode would be IR active.

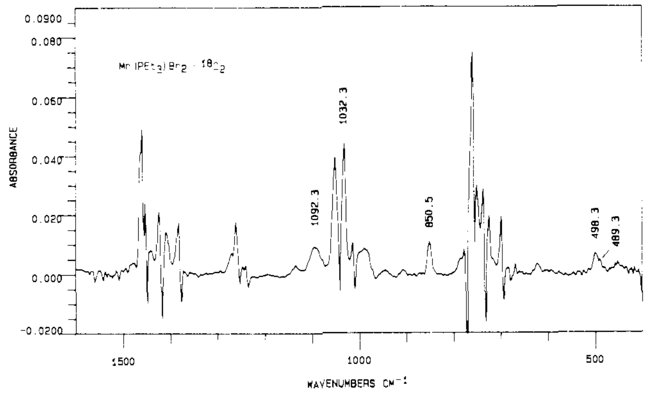

Figure 3. Infrared difference spectrum of the peroxo complex $MnPEt_3Br_2{}^{18}O_2$. A film of $MnPEt_3Br_2$ was exposed to 11 Torr of $^{18}O_2$ for 15 min at -30 °C.

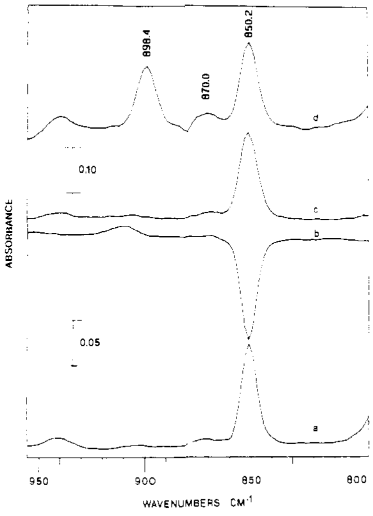

Figure 4. Infrared difference spectra in the O–O stretching region: (a) for the peroxo complex $MnPEt_3Br_2\cdot{}^{18}O_2$ formed after interaction of 11 Torr of $^{18}O_2$ for 4 h at -30 °C minus that for the complex $MnPEt_3Br_2$; (b) following evacuation for 2 h at -30 °C and warming for 1 h to 5 °C under evacuation minus spectrum a; (c) for the peroxo complex $MnPEt_3Br_2\cdot{}^{18}O_2$ formed after interaction of 15.4 Torr of $^{18}O_2$ for 1 h at -30 °C minus that for the complex $MnPEt_3Br_2$; (d) for the mixture of $^{18}O_2$ and $^{16}O_2$ peroxo complexes formed after addition of 15.4 Torr of $^{16}O_2$ to the 15.4 Torr of $^{18}O_2$ present and interaction for 2 h at -30 °C minus that for the complex $MnPEt_3Br_2$.

In another experiment a $MnPEt_3Br_2$ film was exposed to 11 Torr of $^{18}O_2$ at -30 °C for 4 h, subjected to evacuation at -30 °C for 2 h followed by warming to 5 °C over a 1-h period, and then reexposed to 15.4 Torr of $^{18}O_2$ at -30 °C for 1 h, and finally $^{16}O_2$ was added to produce a total pressure of 30.8 Torr ($^{18}O_2$:$^{16}O_2$

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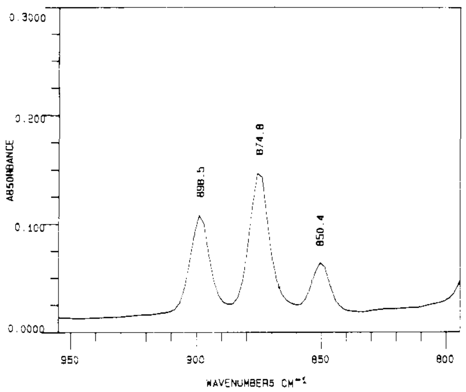

Figure 5. Infrared difference spectrum in the O–O stretching region for a mixture of peroxo complexes of a $MnPEt_3Br_2$ film exposed to a mixture of $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$ at −30 °C (see text).

= 1:1) over a 2-h period at −30 °C. The O–O stretching region of the infrared spectra recorded following each of these operations is shown in Figure 4. Figure 4a illustrates the development of the $^{18}O_2$ peroxo species, Figure 4b its loss upon evacuation, Figure 4c its reappearance, and Figure 4d the formation of a $^{16}O_2$ peroxo species. The $^{18}O_2$ band declined in intensity somewhat during the development of the $^{16}O_2$ band. The two isotopic diatomic oxygen species are thus freely exchanging with the manganese complex. It has been suggested to us that the loss of intensity of the $^{18}O_2$ peroxo band during the development of the $^{16}O_2$ band could be due to decomposition of the peroxo species to a phosphine oxide product rather than to reversible interaction with dioxygen.[16] To evaluate this possibility, we sublimed 100 mg of $MnBr_2$ onto a cold finger of surface area 61.4 cm^2 in a specially designed Dewar, degassed at 10^{-6} Torr, exposed the film to the vapor pressure of triethyl phosphine, evacuated at 10^{-6} Torr for 4 h, and exposed the complex film to 25 Torr of $^{16}O_2$ for 150 min and then 760 Torr for 60 min at −30 °C to produce a deep red color but no measurable pressure drop. Then the oxygenated complex was cooled to −100 °C while the excess O_2 was evacuated (to 10^{-6} Torr); the red color remained. Finally the sample was allowed to warm to ambient temperature, with all desorbed gas (3.5 Torr) being trapped. Mass spectral analysis showed the desorbed gas to be primarily $^{16}O_2$ with a small amount of CO as an impurity from the vacuum system. We believe that this experiment demonstrates conclusively that a reversible interaction of the complex with dioxygen at −30 °C is occurring.

The weak broad feature at ca. 870 cm^{-1} in Figure 4 could be due to an ^{16}O–^{18}O peroxo species, which would be indicative of partial dissociation of dioxygen on manganese. Mass spectrometric sampling of the gases in the cell at −30 °C revealed no m/e = 34 peak indicative of $^{16}O^{18}O$. However, upon warming the sample to ambient temperature during evacuation, an m/e = 34 peak in the mass spectrum appeared and actually eventually exceeded the intensities of the m/e = 36 and m/e = 32 peaks. We found that the cracking pattern for triethylphosphine also contains a large m/e = 34 peak (presumably due to PH_3^+) with our mass spectrometer (Molytek SM 1000M) under similar conditions. Thus the weak infrared band at 870 cm^{-1} may be due to a ligand decomposition product rather than to a $^{16}O^{18}O$ peroxo species. To test these hypotheses, an authentic sample of $^{16}O^{18}O$ was prepared by electrical discharge through a mixture of 11.2 Torr of $^{16}O_2$ and 9.7 Torr of $^{18}O_2$ to produce a mixture containing (mass spectrometric analyses) a ratio of 3.0 parts $^{16}O_2$, 3.45 parts $^{16}O^{18}O$, and 1.0 part $^{18}O_2$. Any ozone produced was removed by condensation on molecular sieves at 77 K. Then 16.5 Torr of this mixture of dioxygen species was interacted with an $MnPEt_3Br_2$ film at −30 °C for 4.5 h, and the infrared spectrum shown in Figure 5 was recorded. It is evident that the authentic $^{16}O^{18}O$ species exhibits its infrared band at 875 cm^{-1}, not at 870 cm^{-1} as for the species represented in Figure 4. Furthermore, the $^{16}O^{18}O$ band in Figure 5 has the same width profile as do the $^{16}O_2$ and $^{18}O_2$ peroxo species bands but unlike the broad profile of the 870-cm^{-1} band in Figure 4. Therefore, we conclude that the 870-cm^{-1} band in Figure 4 refers to a small amount of ligand decomposition product rather than to a $^{16}O^{18}O$ species.

Conclusions

In summary, this work has demonstrated a reversible interaction of dioxygen and $MnPEt_3Br_2$ to form a side-on peroxo species (red) at low temperature (−30 °C). As reported previously,[4] at higher temperature (ambient and above) the interaction of dioxygen, which may or may not be reversible, with the manganese complex film produces a superoxo species (blue), which decomposes irreversibly to an inactive phosphine oxide complex.

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(16) We acknowledge a reviewer for this suggestion.

Chemielectron Spectroscopy: Study of the Ce + O_2 Reaction

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Abstract: The chemielectron and mass-resolved ion spectra produced from the Ce + O_2 reaction have been recorded. The mass spectrum together with approximate thermochemical and kinetic calculations have been used to show that the major chemiionization channel for this reaction under thermal conditions is the associative ionization process, $Ce + O_2 \rightarrow CeO_2^+ + e^-$. The electron spectrum has been interpreted in terms of this process via a classical turning-point mechanism. CeO_2^+ and CeO^+ are observed as reaction products in the mass-resolved ion spectrum. CeO_2^+ arises almost completely from the above associative ionization reaction, whereas CeO^+ is shown to arise from more than one reaction in the Ce + O_2 reaction scheme.

The importance of chemiionization reactions in flames,[1,2] upper atmosphere chemistry,[3] and in shock waves and detonations[4,5] has led to a large number of these reactions being identified in recent years. However, for most of these reactions virtually nothing is known about the mechanism of the ionization process. Many chemiionization reactions produce free electrons whose energy distribution can be measured by electron spectroscopy. These

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