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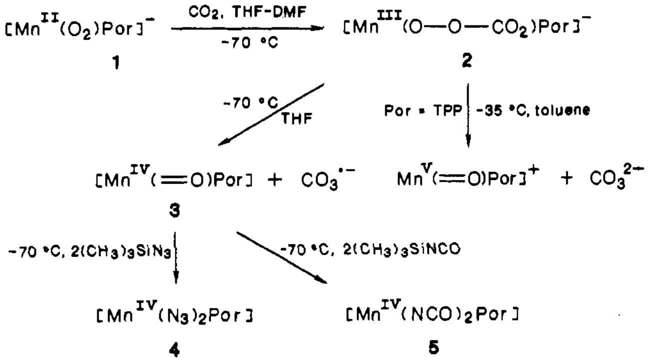
Communications

Formation of Manganese(IV)-Oxo-Porphyrin Derivatives by Decomposition of Peroxycarbonate Complexes

Sir:

We have shown recently that carbon dioxide reacts in tetrahydrofuran (THF) at -70 °C with peroxo-iron(III)-porphyrin derivatives to yield THF adducts of iron(IV)-oxo-porphyrins.[1] The [$Fe^{IV}(=O)$] stretching vibration of the THF and 1-methylimidazole (1MeIm) adducts of [$Fe^{IV}(=O)TP_{piv}P$] ($TP_{piv}P$ = *meso*-tetrakis(α-pivalamidophenyl)porphyrin dianion) obtained by this carbon dioxide reaction have been located respectively at 829 and 807 cm^{-1} by resonance Raman spectroscopy.[2] In the course of our research on the formation of the corresponding manganese(IV)-oxo-porphyrin species we examined the reaction of carbon dioxide with manganese(II)-superoxo complexes, [$Mn(O_2)(porphyrin)]^-$.[3,4] It was shown recently that these superoxo derivatives react with acyl chlorides and acid anhydrides to form manganese(III)-acylperoxo intermediates that undergo at room temperature O-O bond heterolysis to yield manganese(V)-oxo derivatives.[5,6] In this paper, we show that the manganese(III)-peroxycarbonate intermediates formed by the carbon dioxide reaction with manganese(II)-superoxo complexes undergo either O-O bond homolysis into manganese(IV)-oxo species or O-O bond heterolysis into manganese(V)-oxo porphyrin species depending on the solvent or the porphyrin used.

Scheme I



Reaction in THF or toluene of manganese(II) porphyrins, [$Mn^{II}Por$][7] (Por = tetraphenylporphyrin (TPP), tetrakis(pentafluorophenyl)porphyrin (TPFPP) and "picket fence" porphyrin ($TP_{piv}P$) dianions) with 1 equiv of potassium superoxide in dimethylformamide (DMF) or THF containing 18-crown-6 produced at room temperature the corresponding manganese(II)-superoxo derivatives [$Mn^{II}(O_2)Por]^-$ (**1**).[3,4] These complexes **1** react at -70 °C with carbon dioxide to afford the corresponding manganese(III)-peroxycarbonate intermediates [$Mn^{III}(O_2CO_2)Por]^-$ (**2**) (Scheme I). Identification of **2** as a manganese(III)-peroxycarbonate species is based on the following observations: the visible spectra of these compounds are typical for manganese(III) species[8] (for **2**($TP_{piv}P$) in THF or toluene λ_{max} = 370, 400, 464, 525, 580, 615 nm), and these spectra are very similar to the spectrum of the manganese(III)-acylperoxo derivative obtained by Groves et al.[5] Moreover, warming the toluene solutions of **2**(TPP) to -35 °C caused the smooth decomposition of this intermediate to a complex having spectral properties identical with those reported for manganese(V)-oxo-porphyrin derivatives[5,6,9-11] (λ_{max} = 422, 520 nm; Figure 1a). In contrast, in THF the manganese(III)-peroxycarbonate intermediates **2** decompose rapidly at -70 °C with formation of the new species **3**, whose visible spectra present a strong Soret band and a unique band in the α-β region (λ_{max} = 426, 543 nm (**3**(TPP)); 419, 538 nm (**3**(TPFPP)); 436, 552 nm (**3**($TP_{piv}P$))). Direct reaction at -70 °C of chloro-manganese(III) derivatives in THF with potassium peroxycarbonate prepared in DMF also produced **3** (Figure 1b). Identification of **3** as manganese(IV)-oxo-porphyrin derivatives[12] is based on the following observations:[13] (a) **3** reacts with triphenylphosphine in the presence of pyridine to produce triphenylphosphine oxide and the pyridine adducts of the corresponding manganese(II) porphyrins;[7] (b) addition of an excess of methyl alcohol (MeOH) produced the corresponding dimethoxy-manganese(IV) species;[14] (c) oxidation of **3** with bromine

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(13) Since the submission of this paper, low-temperature EXAFS studies have been made on **3**(TPFPP) at LURE, Orsay, France. The energy of the absorption edge is consistent with a manganese(IV) formulation for this species. Furthermore, a preliminary analysis of the data indicates the presence of a short distance of 1.67 ± 0.03 Å, which corresponds undoubtedly to the manganese(IV)-oxo bond: Goulon, J.; Schappacher, M.; Fischer, J.; Weiss, F., to be submitted for publication.

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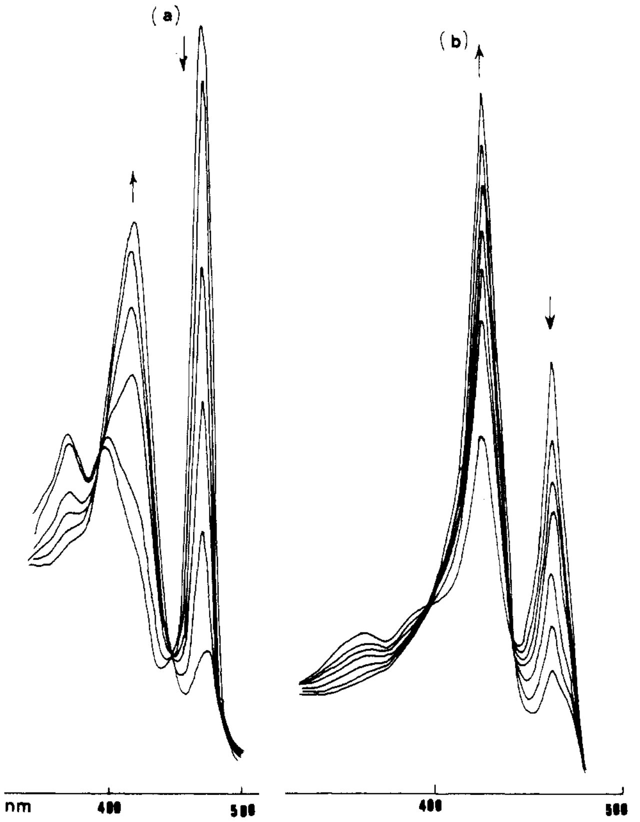

Figure 1. (a) Changes in the electronic spectrum of $[Mn(O_2CO_2)TPP]^-$ (**2**(TPP)) in toluene resulting from an increase in temperature from −70 to −35 °C. (b) Changes in the electronic spectrum of $[Mn^{III}Cl(TPP)]$ upon reaction in THF at −70 °C with potassium peroxycarbonate prepared in DMF.

or phenoxathiine hexachloroantimonate led to species having spectral properties that are indentical with (TPP) or similar to (TPFPP, $TP_{piv}P$) those reported for manganese(V)–oxo–porphyrin species;[5,9–11] (d) the X-band EPR spectra of these species, run at −150 °C in frozen DMF–THF solution present a strong signal at $g \simeq 2$ (**3**(TPP), 2.050; **3**(TPFPP), 2.056 (Figure 2); **3**($TP_{piv}P$), 2.048) and a weaker signal at $g \simeq 4.4$ (**3**(TPP), 4.331; **3**(TPFPP), 4.407 (Figure 2); **3**($TP_{piv}P$), 4.390). It is known that the nature and complexity of frozen-solution d^3 ion EPR spectra depend on the zero-field splitting parameters. When the axial parameter D is small ($2D \ll 0.31$ cm^{-1}), the dominating signal lies at $g \simeq 2$ attended by one or more broad and weak signals at low fields (1000–1500 G).[15,16] The spectra observed for **3** present these characteristics. Thus, they are consistent with the presence of high-spin $S = {}^3/_2$ manganese(IV)[13] porphyrin derivatives. The spectra of different samples of **3**(TPFPP) presented several times an additional weak signal at $g = 6.20$ that showed at 20 K a well-resolved ^{55}Mn six-line hyperfine structure with $A = 85$ G. This high-field signal is probably not due to an $S = {}^3/_2$ manganese(IV) system[17,18] and corresponds most probably to a small amount of a decomposition product that has, so far, not been identified.

Morever, solutions of **3** react instantaneously in THF at −70 °C with trimethylsilyl azide to yield the corresponding manganese(IV)–diazide species **4**[19] (**4**($TP_{piv}P$) $\lambda_{max} = 422, 523$ nm) and with trimethylsilylisocyanate to form the manganese(IV) diisocyanate derivatives[19] **5** (**5**($TP_{piv}P$) $\lambda_{max} = 421, 525$ nm). They react also with (trimethylsilyl)imidazole to yield probably the manganese(IV)–diimidazolate complexes **6**[20] (**6**($TP_{piv}P$) $\lambda_{max} = 420, 522$ nm). Furthermore, **3**(TPFPP) reacts with cyclohexene to give a manganese(II) species and a mixture of cyclohexene oxide (relative yield 40%), cyclohexen-1-ol (30%), and cyclohexen-1-one (30%), identified by GLC.

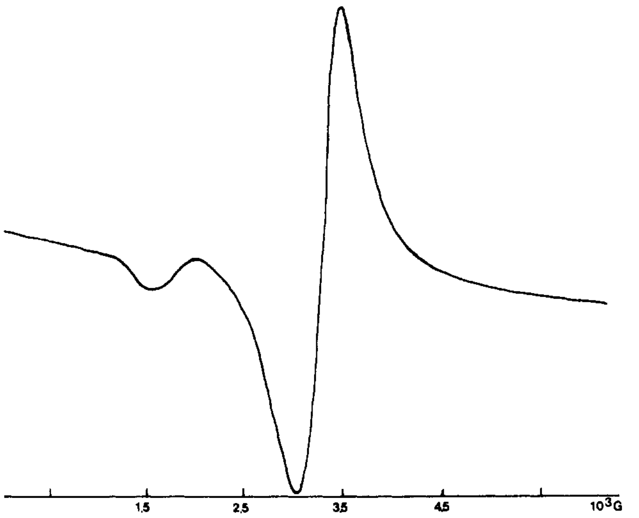

Figure 2. EPR spectrum of $[Mn^{IV}(=O)(TPFPP)]$ (**3**(TPFPP), 10 mmol) in frozen THF–DMF solution ($t = -160$ °C; $\nu = 9.497$ MHz).

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(20) The precise nature of these species **6** is presently under study. The EPR spectrum of **6**($TP_{piv}P$) indicates the presence of a high-spin $S = {}^3/_2$ manganese(IV) derivative.

(21) Laboratoire de chimie des mêtaux de transition et de catalyse associé au CNRS (UA 424).

Institut Le Bel[21]
Universitê Louis Pasteur
67070 Strasbourg, France

M. Schappacher
R. Weiss*

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Synthesis, Structure, and Superconductivity of Single Crystals of High-T_c $La_{1.85}Sr_{0.15}CuO_4$

Sir:

Record high onset superconducting transition temperatures (T_c) of ~30–36 K (at ambient pressure),[1–4] and ~40.2[5a] to 52.5 K[5b] (at pressures to ~12 kbar), have very recently been reported for the La–Ba–Cu–O (LBCO) system. Superconducting T_c's as high as 70 K have been reported in some metastable LBCO samples.[9]

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