An Electron Paramagnetic Resonance Investigation of the Reaction of Some Radical Traps with Oxomanganese Porphyrins

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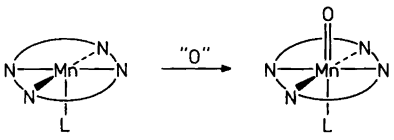
The reaction of 2-methyl-*N*-(phenylmethylene)-2-propanamine *N*-oxide, 2-methyl-2-nitrosopropane and nitrosobenzene with manganese(III) porphyrins and an oxygen donor system (iodosylbenzene or sodium hypochlorite/phase-transfer catalyst) has been studied using electron paramagnetic resonance investigations. In the reaction of 2-methyl-*N*-(phenylmethylene)-2-propanamine *N*-oxide with the oxomanganese porphyrin a *t*-butyl radical is generated which is trapped by 2-methyl-*N*-(phenylmethylene)-2-propanamine *N*-oxide; furthermore an acylaminoxyl radical is also observed. The reaction of 2-methyl-2-nitrosopropane and nitrosobenzene with the manganese (III) porphyrins and the oxygen donor system generates the corresponding di-*t*-butyl- and diphenyl-aminoxyl radicals, respectively; in the case of 2-methyl-2-nitrosopropane as the substrate an acylaminoxyl radical is also detected. The reaction of 2-methyl-2-nitrosopropane and nitrosobenzene also produces radicals whose spectrum can be interpretated as being due to a *para*-aryl substituted *t*-butylaminoxyl and probably a *para*-hydroxyarylaminoxyl coupled to the *para*-position of an aryl group, respectively. These results could be indications that the phenyl group in the manganese porphyrin might be attacked during the reaction. The formation of radicals in the reactions can be suppressed by the addition of nitrogenous ligands such as imidazole or pyridine to the reaction mixture leading to an EPR-silent reaction. The results are discussed in relation to a Por-Mn(IV)–O· radical type of intermediate rather than Por-Mn(V)=O in an attempt to account for the radicals observed in these reactions.

The interest in understanding the properties of cytochrome P-450, peroxidase and catalase has stimulated wider interest for the properties of metalloporphyrins.[1] In particular, metalloporphyrins with manganese(III)[2] and iron(III)[3] as the metal have often been used as model systems for enzymatic reactions. Recently a relationship has become apparent between enzymology and homogeneous catalysis as manganese and iron porphyrins have been shown to act as catalysts for the oxidation of a variety of organic substrates with different types of oxygen donor.[1-4] The manganese(III) porphyrins have been shown to catalyze the oxidation of alkanes, alkenes, nitrogen and sulphur containing compounds using oxygen donors such as iodosylbenzene, sodium hypochlorite, molecular oxygen in the presence of a reductant, alkyl and hydrogen peroxides and amine *N*-oxides.[1-4] In the manganese(III) porphyrin-catalyzed reactions nitrogenous axial ligands, as e.g. imidazole or pyridine, have a profound effect on the reaction rate, catalyst stability, and product stereochemistry.[1c,d,f,2j,l,5]

The first step in the reaction between the manganese(III) porphyrins, **1** and an oxygen donor is the formation of an oxomanganese porphyrin species, **2**, [reaction (1)], followed by the transfer of the oxygen atom from **2** to the substrate. The exact structure of **2** is unknown owing to its



1 **2** (1)

instability, but recently an oxomanganese(V) complex with 1,2-bis(2-hydroxy-2-methylpropanamido)benzene as the ligand has been characterized by X-ray crystallographic investigations[6] and shows a similar oxomanganese structure as that suggested for **2**. The electronic structure of **2** has been discussed in terms of a high degree of triplet character in the ground state represented as Por-Mn(IV)–O·, rather than Por-Mn(V)=O, where the latter represents the singlet state.[2j] The radical character of the oxomanganese porphyrin has e.g. been suggested on the basis of the loss of stereochemistry in the epoxidation of *Z*-alkenes and the hydroxylation of alkanes.[1c,f,2] However, it should be noted that the stereochemistry in the epoxidation reaction of *Z*-alkenes can to a high degree be maintained by the addition of nitrogenous ligands.[1c,f,2c,d,h,j,k,5]

In this paper we present an electron paramagnetic resonance (EPR) investigation of the reaction of some typical radical traps with manganese(III) porphyrins and iodosylbenzene or sodium hypochlorite/phase-transfer as the oxygen donor to show that the oxomanganese porphyrins

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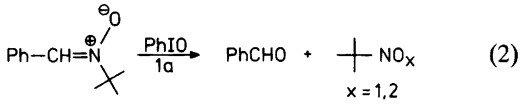
formed initiate radical reactions. The work presented here is to our knowledge the first time radical reactions have been investigated by means of EPR spectroscopy in the reaction of manganese(III) porphyrins with oxygen donors.[7] The radical traps used are 2-methyl-*N*-(phenylmethylene)-2-propanamine *N*-oxide (PBN), 2-methyl-2-nitrosopropane (NtB) and nitrosobenzene (NBz).[8,9]

Results and discussion

Reaction of PBN with iodosylbenzene in the presence of chloro-[(5,10,15,20)-tetraphenylporphyrinato]manganese (III), **1a**, in dichloromethane gives the following main reaction at room temperature [reaction (2)]. The reaction gives

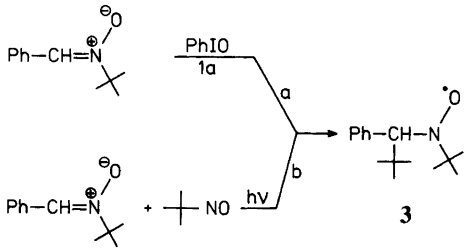


(2)

28 % of benzaldehyde after 3 h. Similar results to those in reaction (2) are also obtained with sodium hypochlorite/tetrabutylammonium chloride as the oxygen donor system.

Examination of reaction (2) by EPR spectroscopy revealed two radical species. The EPR spectrum of the first radical formed is depicted in Fig. 1(a) and shows the typical nitrogen and β-H couplings of a radical trapped by PBN.[8–10] The EPR spectrum shown in Fig. 1(a) is simulated to have two hyperfine splittings of a_N = 13.51 G and a_H = 1.61 G. It is interesting to note that the addition of imidazole or pyridine to the reaction leads to an EPR silent reaction {[**1a**]:[imidazole] = 1:10 in Fig. 1(b)}.

A radical with the same EPR data as that shown in Fig. 1(a) is generated by photolysis of NtB in the presence of PBN in dichloromethane [reaction (3b)].[10] It thus appears that the reaction of PBN with iodosylbenzene or sodium hypochlorite/tetrabutylammonium chloride in the presence of **1a** probably leads to the formation of a *t*-butyl radical which is trapped by PBN [reaction (3a)].



(3)

The radical **3** disappears gradually and a new radical is formed [Figs. 1(c, indicated with arrows), (d)] with a hyperfine splitting of 7.94 G which could be an indication of an acylaminoxyl radical (*vide infra*).[11] It should be noted that the reaction of PBN with **1a** in the absence of iodosylbenzene gives no EPR signal. The same radicals as those shown in Figs. 1(a) and 1(d) are also formed when chloro-[(5,10,15,20)-tetra(*p*-chlorophenyl)porphyrinato]manganese(III), **1b**, and chloro[(5,10,15,20)-tetra(*p*-methoxyphenyl)porphyrinato]manganese(III), **1c**, are used as catalysts with iodosylbenzene or sodium hypochlorite/tetrabutylammonium chloride as oxygen donors.

The reaction of NtB with iodosylbenzene in the presence of **1a** in dichloromethane affords 2-methyl-2-nitropropane as the main product.[4c] A similar result is obtained with

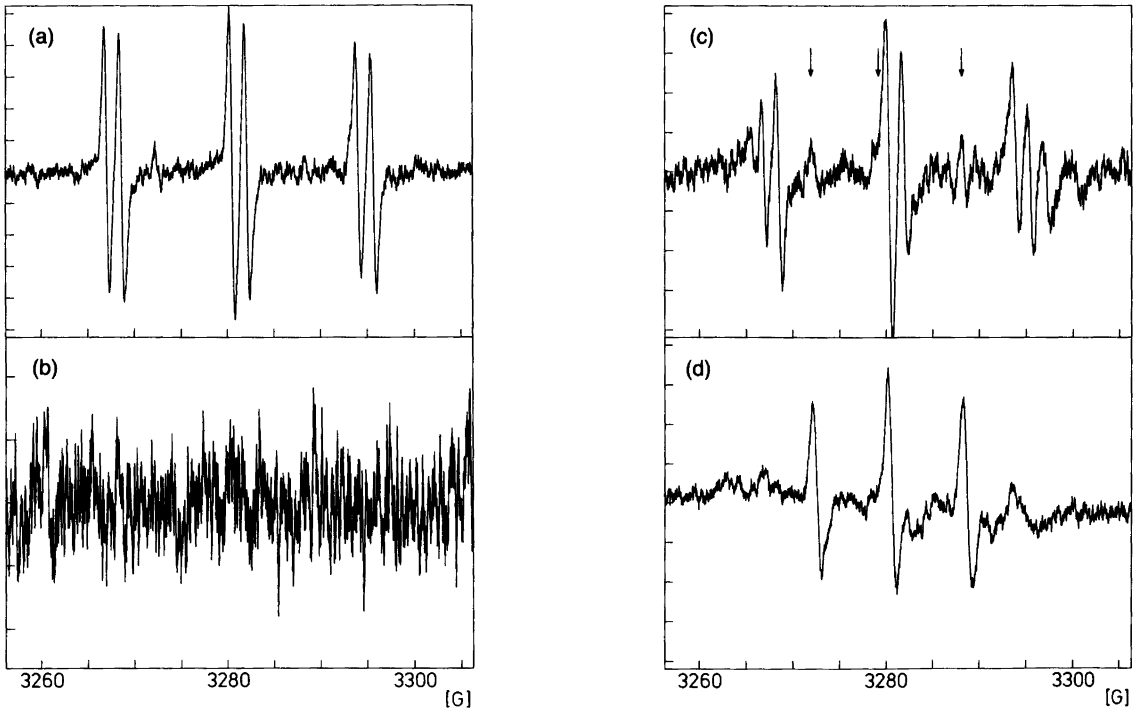


Fig. 1. (a) EPR spectrum of the reaction of PBN, PhIO and **1a** (ca. 2 min after mixing); (b) EPR spectrum of the reaction of PBN, PhIO, imidazole and **1a** (ca. 5 min after mixing); (c) as (a) after ca. 15. min; (d) as (a) after ca. 30 min.

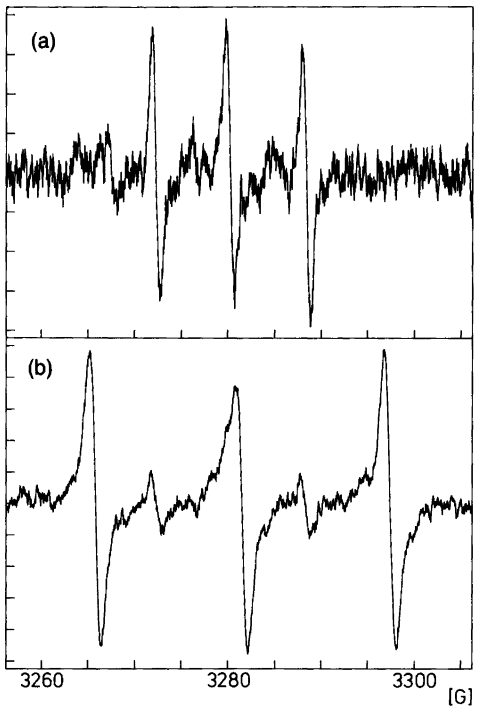
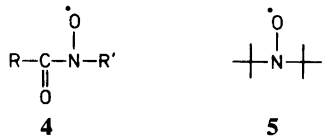


Fig. 2. (a) EPR spectrum of the reaction of NtB, PhIO and **1a** (ca. 1 min after mixing); (b) as (a) after ca. 5 min.

sodium hypochlorite/tetrabutylammonium chloride as the oxygen donor system.[4c] EPR spectroscopic monitoring revealed the formation of radicals in the reaction of Ntb with iodosylbenzene or sodium hypochlorite/tetrabutylammonium chloride in the presence of **1a** as the catalyst. Two types, shown in Figs. 2(a) and 2(b), are generated within a few minutes after the addition of iodosylbenzene to NtB and **1a** in dichloromethane.

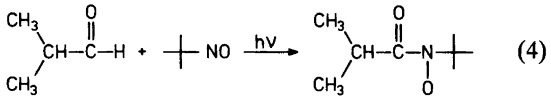
The two radicals shown in Figs. 2(a) and 2(b) have hyperfine splittings of 7.94 and 15.75 G, respectively, indicating two aminoxyl radicals. The radical with a_N = 7.94 G seems to be the same as that formed in the reaction of PBN with the **1a**/iodosylbenzene system, and could be an acylaminoxyl radical, **4**.[11] The other radical with a_N = 15.75 G corresponds to di-*t*-butylaminoxyl (**5**).[12]



4 **5**

The radical **4** (a_N = 7.94 G) disappears gradually and the signal for **5** (a_N = 15.75 G) increases [Fig. 2(b)]. The formation of the radicals detected by EPR spectroscopy can here also be eliminated by addition of imidazole or pyridine to the reaction mixture in the ratio [**1a**]:[imidazole/pyridine] = 1:10.

The radical **4** which is formed in the reaction of both PBN and NtB with the **1a**/oxygen donor system could then probably originate from the *t*-butyl group. We have found that a radical with similar a_N value corresponding to **4** can be generated by photolysis of 2-methylpropanal in the presence of NtB [reaction (4)],[11b] which could be an indication that the R′ group in **4** is a *t*-butyl group. Another possibility for the formation of the aminoxyl radical in the reaction with PBN as the substrate is oxidation of PBN to $PhC(O)N(O^{\cdot})C(CH_3)_3$.



(4)

After prolonged reaction time (> 15 min) in the EPR spectrometer the two EPR signals originating from **4** and **5** disappear and a new signal, shown in Fig. 3(a), emerges. This signal was simulated as shown in Fig. 3(b) and good agreement between the experimental and the simulated spectra is observed. The simulated spectrum might correspond to a *para*-substituted aryl(*t*-butyl)aminoxyl radical with a_N = 15.10 G, a_H^o = 1.57 G and a_H^m = 0.71 and 0.95 G.[13] The radical species giving rise to the EPR spectrum in Fig. 3(a) *could be* the one shown in **6**. This is in line with the substantial perturbation from the heavy porphyrin moiety on the aryl protons making them non-equivalent at the *meta*-positions. The structure shown in **6** is with only one *t*-butylaminoxyl group present, but more than one might also be possible.

To investigate whether the *para*-position in the phenyl group in **1a** is involved in the reaction, we used **1c** as the

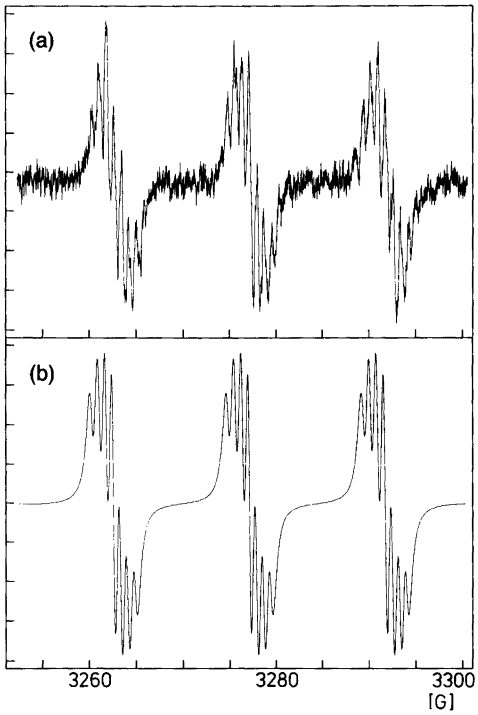
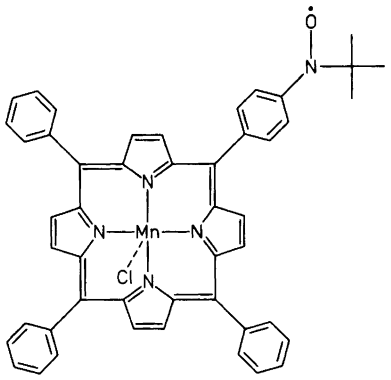


Fig. 3. (a) EPR spectrum of the reaction of NtB, PhIO and **1a** (ca. 30 min after mixing); (b) simulated spectrum.



6

catalyst with iodosylbenzene as the oxygen donor and NtB as the substrate. Under similar reaction conditions only the radicals shown in Fig. 2 were observed. This supports the interpretation of the spectrum shown in Fig. 3(a) as one in which the *para*-position of the phenyl group in the catalyst is substituted with an *N*-oxide group, although we cannot exclude the possibility that the radical shown in Fig. 3(a) is of a type other than that outlined in **6**.

Reaction of NBz with **1a** as the catalyst and iodosylbenzene as the oxygen donor system gives nitrobenzene as the main product.[4c] However, in the EPR spectrum two types of radical are observed. The first radical formed was simulated and corresponds to the diphenylaminoxyl radical (not shown here).[10a] The diphenylaminoxyl radical is observed for about 30 min. Along with the diphenylaminoxyl radical another radical is also formed as shown in Fig. 4(a). The spectrum of this radical exhibits considerably asymmetric line broadening, and a satisfactory match between the experimental and the simulated spectrum cannot be obtained with the assumption of constant linewidth to all lines. It is well known that these linewidth variations are derived from a coupling between the Brownian motion of the radical and the anisotropies in the g and hyperfine tensors. From the general theory of magnetic relaxation, the linewidths of lines exhibiting the effect of slow tumbling are given by eqn. (5)[14] where M_i and M_j are the total

$$L_w = A + \sum_i B_i M_i + \sum_i C_i M_i^2 + \sum_{i<j} D_{ij} M_i M_j \qquad (5)$$

z-components of the nuclear spin quantum number for the sets i and j of completely equivalent nuclei, and the summation is over all sets. A is the constant broadening given to all lines. B_i are the coefficients giving asymmetric broadening and arise from the product of the g and the hyperfine tensors. C_i and D_{ij} are single functions of the hyperfine anisotropy; D_{ij} arises from products between nuclei of different sets.

We have incorporated the above linewidth equation into our simulation procedure and obtained 'best fit' hyperfine constants as well as linewidth parameters by an iterative optimization procedure described previously.[15] The final simulation is shown in Fig. 4(b). We observe a close match between the experimental and the simulated spectrum. The data obtained from the simulation are: a_N = 10.09 G, a_H^o = 2.43 G, a_H^o = 2.30 G, a_H^p = 0.89 G, a_H^m = 0.71 G, a_H^m = 0.71 G, where the figures shown for the *ortho*- and *meta*-positions are average values for the pair of hydrogens. These simulations indicate that two aromatic groups might be present. For a hydrogen in a *para*-position one would expect a splitting of about 2.4 G. However, only a reduced splitting of 0.89 G is observed which could be derived from the presence of a hydroxy hydrogen. To account for this, hydroxylation of the phenyl group at the *para*-position must then have taken place. It is proposed that the radical shown in Fig. 4(a) *might correspond* to that shown in **7**. Both the hydroxy group and the porphyrin affect the tumbling rate of the aminoxyl radical.[16]

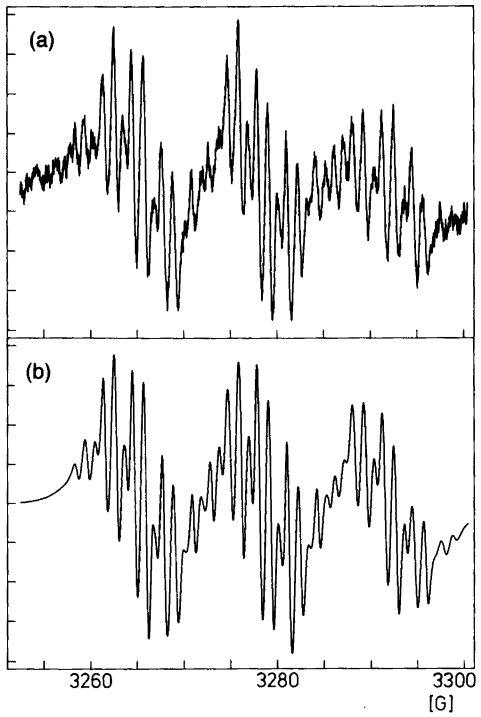
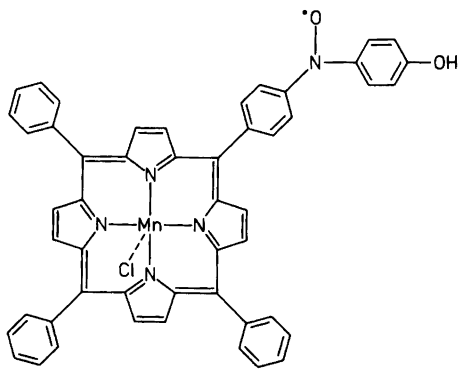


Fig. 4. (a) EPR spectrum of the reaction of NBz, PhIO and **1a** (ca. 30 min after mixing); (b) simulated spectrum.



7

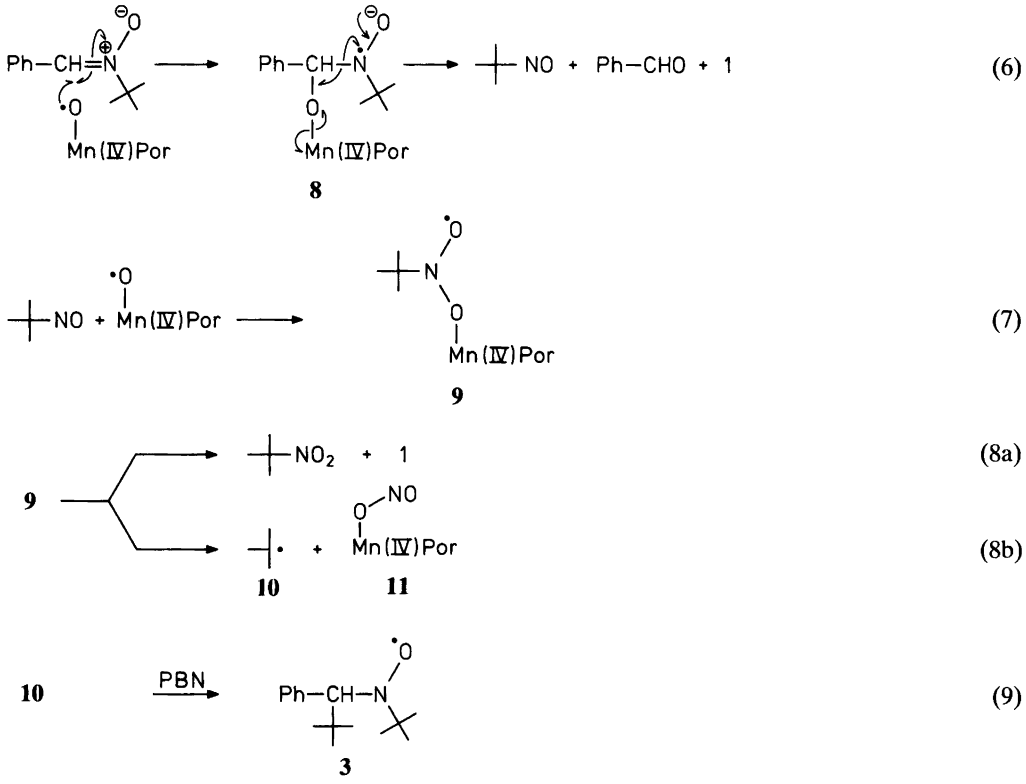
The formation of the radicals in the reaction of NBz with iodosylbenzene in the presence of **1a** as the catalyst is also affected by the presence of imidazole or pyridine during the reaction in the same way as for the other reactions above.

Discussion

The results above show that PBN, NtB and NBz and an oxygen donor system, with manganese(III) porphyrins as the catalyst, are able to generate different radicals which can be detected by EPR spectroscopy. It is also observed that the formation of the radicals is very dependent on coordinating nitrogen ligands, as the presence of imidazole or pyridine during the reaction course leads to an EPR-silent reaction.

The reaction of PBN with the oxygen donor in the presence of **1a** as the catalyst leads to the formation of benzaldehyde, NtB and 2-methyl-2-nitropropane [reaction (2)]. A tentative mechanism is outlined in Scheme 1 which accounts for some of the observed radicals for a Por-Mn(IV)–O· type of intermediate. The first step in this reaction is an attack of the oxygen in the oxomanganese porphyrin at the carbon atom in the –CH=N< function in PBN leading to **8**, from which benzaldehyde, NtB and **1** can be formed as shown. The NtB, formed in reaction (6), might then react with the oxomanganese porphyrin with formation of **9** [reaction (7)]. From the intermediate **9** two possibilities can be envisaged, either a homolytic cleavage of the Mn–O bond leading to 2-methyl-2-nitropropane [reaction (8a)] or a homolytic cleavage of the C–N bond leading to a *t*-butyl radical, **10** and a nitrite–manganese porphyrin, **11** [reaction (8b)]. The *t*-butyl radical is then probably trapped by PBN leading to **3** [eqn. (9)] [the EPR spectrum is shown in Fig. 1(a)]. To account for the acylaminoxyl radical, **4**, at least three different reaction paths can be considered: (i) the *t*-butyl radical, **10**, formed in reaction (8b) is oxidized to an acyl group and trapped by NtB, (ii) oxidation of the methyl groups in PBN and trapping by NtB or (iii) an oxidation of PBN to $PhC(O)N(O^{\cdot})C(CH_3)_3$.

With NtB as the substrate, intermediate **9** [reaction (7)] is probably also formed followed by the two homolytic fissions outlined in reactions (8a) and (8b). The *t*-butyl radical formed [reaction (8b)] can undergo different reactions: reaction with NtB (because of its much higher concentration compared with the reaction where PBN is the substrate) leads to di-*t*-butylaminoxyl, **5** [Fig. 2(b)]. The acylaminoxyl radical, **4**, shown in Fig. 2(a) can, for example, be formed by oxidation of one of the methyl groups followed by trapping of NtB. The third type of radical formed, suggested to be a *para*-phenyl substituted *t*-butylaminoxyl radical of the manganese porphyrin, **6**, is interesting, as such a radical is probably formed by a hydrogen abstraction from the *para*-position in **1a**, followed by cage escape of this radical and trapping by NtB. The presence of an aryl radical indicates that a species activating



Scheme 1.

enough to break an aryl C–H bond must be present;[17] this species could be the oxomanganese porphyrin in its radical form [Por-Mn(IV)–O·] which leads to a hydroxymanganese (IV) intermediate. The latter intermediate has been suggested on basis of the observation of a monomeric manganese(IV) porphyrin intermediate by EPR spectroscopy during the reaction of $[ClMn(IV)TTP(OIPh)]_2O$ with alkanes.[2i] The absence of an EPR spectrum similar to that shown in Fig. 3, when changing the catalyst to **1c**, supports the idea that the phenyl group in **1a** is involved in the reaction pattern as suggested here.

Changing the *C*-nitroso compound to NBz leads to the same two reaction types as with NtB as the substrate; formation of a diphenylaminoxyl radical and probably the *para*-hydroxy aryl analogue of **6** shown in **7**. The reaction probably takes place via the phenyl analogue of **9**, from which nitrobenzene or a phenyl radical and **11** are formed [compare with reactions (8a) and (8b)]. The phenyl radical is trapped by reaction with NBz, leading to the diphenylaminoxyl radical. An EPR spectrum [Fig. 4(a)] comparable to that obtained with NtB as the substrate [Fig. 3(a)] is also obtained. This spectrum is suggested to originate from the *para*-hydroxyaryl analogue of **6**, e.g. formed in a way similar to that outlined for **6** above, followed by hydroxylation of the *para*-position of the aryl group.

The nitrogenous ligands have a substantial effect on the formation of the radicals, as the presence of ten equivalents or more of imidazole or pyridine relative to the catalyst leads to an EPR-silent reaction. The effect of these nitrogenous ligands on the oxomanganese porphyrin complex might be that a change in the nature of the oxomanganese function occurs from radical-like, Por-Mn(IV)–O·, to closed-shell-like, Por-Mn(V)=O. *Ab initio* theoretical calculations indicate that the main changes in the oxomanganese function, in the presence of pyridine as an axial ligand, are that the oxygen becomes more electrophilic, and that the Mn–O bond length increases while the Mn–O bond order decreases, relative to chloride as ligand.[5f,18] However, these changes probably do not account for the change in reaction path in the present studies. *We therefore propose that the nitrogenous ligands can change the electronic state of the oxomanganese function in oxomanganese porphyrins from radical-like [Por-Mn(IV)–O·] to closed-shell-like [Por-Mn(V)=O].* Such a change in nature of the oxomanganese porphyrin might also account for the change in stereoselectivity in the epoxidation of alkenes when nitrogenous ligands are present during the reaction.[1c,f]

This study shows some new aspects of manganese porphyrins and an oxygen donor in the presence of spin traps: (i) they are able to generate a series of radicals which can be observed by EPR spectroscopy and (ii) the formation of the radicals can be suppressed by the presence of nitrogenous ligands.

Experimental

All spectra were recorded at X-band at room temperature on a Bruker ER 200 spectrometer with a modulation frequency of 25 kHz and an amplitude of about 100 mG. The spectra were stored as 4K discrete points and simulated on a Vax 6210 computer. 'Best fits' were obtained by means of an iterative optimization procedure.[15]

Chloro-(5,10,15,20-tetraphenylporphyrinato)manganese-(III), **1a**, nitrosobenzene, tetrabutylammonium chloride and sodium hypochlorite were purchased and used as received. The *para*-chloro and *para*-methoxy analogues of **1a**,[2j] 2-methyl-*N*-(phenylmethylene)-2-propanamine *N*-oxide[19] and 2-methyl-2-nitrosopropane[20] were prepared according to the literature. Iodosylbenzene was prepared from iodobenzene diacetate.[3c] Dichloromethane (Merck, *pa*) was refluxed for 2 h in the presence of $KMnO_4$ and then destilled three times before use.

General procedure for the EPR studies. Fifty μl of **1** (2.5 mM in CH_2Cl_2), 50 μl of PBN, NtB or NBz (25 mM in CH_2Cl_2 kept in the absence of light) and 100 μl of a 100 mM suspension of PhIO in CH_2Cl_2 were mixed in an EPR glass tube and monitored by EPR spectroscopy.

The reactions in the presence of imidazole or pyridine were carried out in a similar way, as above, with the addition of 50 μl 25 mM of the nitrogenous ligands to the reaction mixture.

The reactions with NaOCl as the oxygen donor were also carried out as above, but with a 100 μl 15 % NaOCl solution and a 0.1 M $(C_4H_9)_4NCl$ solution as the phase-transfer catalyst.

Photochemical reactions. Fifty μl of PBN (25 mM in CH_2Cl_2) and 10 μl of NtB (25 mM in CH_2Cl_2) were mixed in an EPR glass tube and irradiated for ca. 15 s as described elsewhere[10] and then monitored by EPR spectroscopy.

Fifty μl of 2-methylpropanal (25 mM in CH_2Cl_2) and 20 μl of NtB (25 mM in CH_2Cl_2) were mixed in an EPR glass tube and irradiated for ca. 15 s as described elsewhere[11b] and then monitored by EPR spectroscopy. This reaction gives **5** as the major product together with **4**.

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