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Oxygen Atom Transfer in the Oxidation of Triphenylphosphine by μ-Oxo-bis[phthalocyaninatoiron(III)]

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It has been shown that μ-oxo-bis[phthalocyaninatoiron(III)] can oxidize triphenylphosphine to triphenylphosphine oxide in the presence of pyridine under mild conditions, resulting in the formation of the corresponding Fe^{II}-bis adduct; this reaction is a rare example of O atom transfer by a μ-oxo Fe^{III} oligomer.

Recently[1] we have described a solid, air stable, crystalline modification of a μ-oxo species of formula $[PcFe]_2O$ (**1**) (Pc = phthalocyaninato dianion), reproducibly obtained by the interaction of FePc suspended in dimethylformamide, dimethylacetamide, tetrahydrofuran, or dioxane with molecular oxygen. Characterization of this crystalline modification, (**1**), to be distinguished from a different crystalline modification of $[PcFe]_2O$ which has been fully characterized,[2] was based on gas-volumetric measurements, i.r. spectra (characteristic bands at 852 and 824 cm^{-1}, $\nu_{as.}$ Fe–O–Fe), and its magnetic behaviour.

$[PcFe]_2O$

(**1**)

On prolonged contact with pyridine (py) (liquid or vapour) in air at room temperature, (**1**) is transformed to $PcFe(py)_2$, with the release of an O atom. This reaction is unusual since the reverse process, equation (1), is normally observed, under

$$2PFeL_2 \xrightarrow{O_2} PFe\text{–}O\text{–}FeP \qquad (1)$$

P = porphyrin, L = *N*-base.

the same experimental conditions, for porphyrin complexes, and iron(II) complexes with related donor ligands such as Schiff bases, ethylenediaminetetra-acetic acid, and other N_4-macrocycles.[3] Interest in oxo complexes (M=O) of transition metals is expanding owing to their use as oxygen transfer agents in the selective oxidation of organic substrates[4] and as postulated intermediates in biological processes.[4b,5] We have therefore undertaken a more detailed investigation of the behaviour of (**1**) in pyridine and have examined the possibility of the oxidation of PPh_3 to $OPPh_3$ by this complex.

Experiments carried out at room temperature and pressure in a gas-volumetric apparatus using a suspension of (**1**) (3 g) in pure pyridine (25 cm^3) gave no evidence of significant dioxygen evolution (volume variations less than 5% of the expected value, *ca.* 30 cm^3). Thus, the conversion of the μ-oxo species into $[PcFe(py)_2]$ does not follow equation (2). This result was given further support by an experiment carried out with a sample of (**1**) isotopically enriched with ^{18}O. $[^{18}O]$(**1**)

$$2[PcFe]_2O \xrightarrow{py} 4[PcFe(py)_2] + O_2 \qquad (2)$$

was prepared in dimethylformamide by the interaction of FePc with O_2, 99% enriched in ^{18}O.[1] The complete disappearance of the bands at 852 and 824 cm^{-1} ($\nu_{as.}$ Fe–^{16}O–Fe) in the i.r. spectrum and the appearance of one strong absorption at 806 cm^{-1} ($\nu_{as.}$ Fe–^{18}O–Fe) ensured that the enrichment of ^{18}O in (**1**) was at least 90%.[1,2] $[^{18}O]$(**1**) and liquid pyridine were placed in a closed apparatus in the presence of air for 48 h to ensure the complete transformation of the μ-oxo species into the bis-adduct. The pyridine vapour was condensed in a cold finger and mass spectral analysis showed the absence of detectable amounts of $^{18}O_2$, thus definitely excluding the possibility that release of the O atom by (**1**) leads to the formation of molecular oxygen, as in equation (2). Visible spectral measurements in pyridine at 30 °C show that the conversion of the μ-oxo species into the bis-pyridine adduct occurs quantitatively {time required 24 h; initial concentration of (**1**): 0.98×10^{-4} M; expected $[PcFe(py)_2]$ (ϵ 1.30×10^5)[6]: 1.96×10^{-4} M; found: 1.95×10^{-4} M}. These data indicate that the $Fe^{III} \rightarrow Fe^{II}$ reduction process does not result in the oxidation of the phthalocyanine chromophore, *i.e.* O atom transfer does not take place internally to the phthalocyanine molecule. Instead, donation occurs to an external substrate, *i.e.* pyridine or any reactive impurity present in this solvent. The difficulties encountered in the identification of the oxidized species in this medium (probably a mixture of different products) led us to use PPh_3 as an oxidizable substrate, as it gives a unique oxidation product, $OPPh_3$, which is easily detectable by i.r. spectra.[4a,b]

When (**1**), suspended under N_2, at room temperature, in a solution of PPh_3 (molar ratio 1 : 1) in toluene and pyridine (a large excess of the latter with respect to the amount calculated for the formation of the bis-adduct) is stirred for 48 h, the reaction shown in equation (3) takes place. At the end of the reaction the bis-pyridine adduct was separated easily by filtration and identified by its i.r. and *X*-ray powder spectra. The toluene solution was evaporated to dryness and the i.r. spectra (Nujol mull) of the solid residue examined in the region 850—650 cm^{-1}, where $OPPh_3$ has a characteristic band at 720 cm^{-1}.[7] The amounts of $OPPh_3$ and residual PPh_3 were estimated by measuring the relative peak height of the 720 and 695 cm^{-1} bands and comparing this with that observed for the same bands in reference spectra obtained from known mixtures of $OPPh_3$ and PPh_3 (error ± 5—10%). Evaluation of the i.r. spectral data of several experiments carried out under identical reaction conditions indicated that reaction (3) goes to completion. Parallel blank experiments showed that partial oxidation of PPh_3 does occur, even in the absence of (**1**); however, the amount of the $OPPh_3$ formed does not exceed the estimated error in the i.r. spectral determinations. On changing the molar ratio of (**1**) : PPh_3 to 1 : 2 it was observed that only *ca.* 50% of the phosphine was converted into the corresponding oxide. These data clearly indicate that the reaction involves the donation of the oxygen atom from (**1**) to PPh_3. Further support for this was obtained by allowing [^{18}O](**1**) to react with PPh_3 (1 : 1 molar ratio). The i.r. spectra of the oxidized phosphine indicated the presence of both $^{18}OPPh_3$ [$\nu(P\text{–}^{18}O)$ 1164 cm^{-1}] and $^{16}OPPh_3$ [$\nu(P\text{–}^{16}O)$ 1194 cm^{-1}] with the former predominating. Examination of the mixture by mass spectra gave 75% of $^{18}OPPh_3$ and 25% of $^{16}OPPh_3$. The amount of $^{18}OPPh_3$ can be increased to 85—90% if the small percentage of PPh_3 oxidized to $^{16}OPPh_3$ in a parallel blank experiment is taken into account. These data are highly satisfactory when considering that ^{18}O transfer takes place from $^{18}O_2$ to $^{18}OPPh_3$, with the intermediate formation of [^{18}O](**1**), *via* two distinct reactions.

$$[PcFe]_2O + PPh_3 \xrightarrow{py} 2[PcFe(py)_2] + OPPh_3 \qquad (3)$$

From the above results it can be conclusively established that the single O atom of (**1**) is stoicheiometrically transferred to PPh_3. To our knowledge, this is the first example of such a reaction for a μ-oxo Fe^{III} oligomer. Since (**1**) is formed by O_2 uptake, even from the air, at room temperature and pressure,[1,2] it can be concluded that mild conditions are required for the overall process [equation (4)].

$$2FePc \xrightarrow{O_2} (\mathbf{1}) \xrightarrow[PPh_3]{py} 2[PcFe(py)_2] + OPPh_3 \qquad (4)$$

We are currently investigating the kinetics and mechanism of this process in order to establish whether O atom transfer is direct or, an unstable intermediate, similar to the 'oxenic' form postulated for the reaction of FePc with O_2 in dimethyl sulphoxide,[8] is the true active agent in this process.

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