

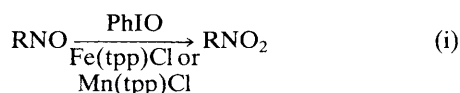
Transition Metal Porphyrins as Catalysts in the Oxidation of Nitroso Compounds

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Iron(III) and manganese(III) porphyrins are found to be very effective catalysts for the oxidation of nitroso to nitro compounds, even at -78°C .

Transition metal porphyrins (especially Mn and Fe), as catalysts for oxygen transfer oxidations, have recently been studied extensively in attempts to understand the mechanisms of the peroxidase and cytochrome P-450 enzymes.¹ Oxo-iron(III) and -manganese(III) porphyrin systems have provided new approaches to oxygen insertion into C–H bonds and stereoselective epoxidation.^{1b,2} Recently it has been shown that iron(III) porphyrin can also catalyse the oxidation of *t*-butyl alcohol to *t*-butyl hydroperoxide.³ This communication describes the use of both iron(III) and manganese(III) porphyrins [chloro-(5,10,15,20-tetraphenylporphyrinato)-iron(III) and -manganese(III), ([Fe(tpp)Cl] and [Mn(tpp)Cl]) as effective catalysts for the oxidation of nitroso compounds to their nitro analogues, even at -78°C [reaction (i)].



R = Ar or *t*-butyl

The formation of nitrobenzene[†] from treatment of nitrosobenzene (1 mmol) and iodosylbenzene (4 mmol) in CH_2Cl_2 (5 ml) with or without Fe(tpp)Cl (0.03 mmol) under various

conditions is shown as a function of time in Figure 1. Nitrobenzene is formed in more than 90% yield within a few minutes, even at -78°C , when Fe(tpp)Cl is present, whereas without Fe(tpp)Cl conversion is minimal.

Treatment of other aromatic nitroso compounds (*e.g.* *o*- and *p*-methoxy-, *p*-dimethylamino-, and *p*-bromo-nitrosobenzene) under the same conditions (0°C) also gave high yields

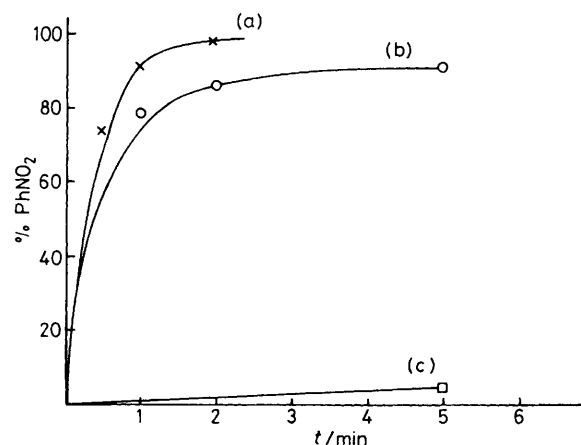
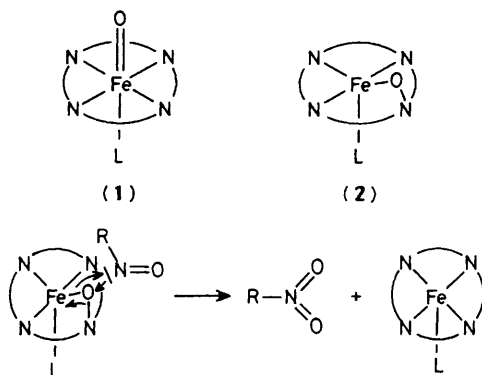


Figure 1. Formation of nitrobenzene from nitrosobenzene as a function of time. (a) PhIO/Fe(tpp)Cl, 0°C ; (b) PhIO/Fe(tpp)Cl, -78°C ; (c) PhIO, 0°C .

[†] The formation of nitrobenzene was followed by g.l.c. (HP 5890; methylsilicone; column temp., 60°C for 5 min, then to 180°C at $8^{\circ}\text{C min}^{-1}$; retention times: PhNO 3.48; PhNO₂ 8.20 min).



Scheme 1

(>80%)‡ of the corresponding nitro analogues within a few minutes. A tertiary aliphatic nitroso compound (Bu^tNO) was also oxidized to the nitro compound in a few minutes in good yield (75%).

Several reagents (e.g. nitric acid, hydrogen peroxide, permanganate, persulphates, and peroxy acids) are able to oxidize nitroso compounds to nitro compounds,⁴ but these reactions often lead to several products. For example nitric acid converts nitrosobenzene into nitrobenzene, *p*-dinitrosobenzene, *p*-nitrophenol, 2,4-dinitrophenol, picric acid, and oxalic acid,⁵ whereas in the oxidization of nitrosobenzene with iodosylbenzene catalysed by Fe(tpp)Cl only nitrobenzene is observed. The present procedure is very mild and selective compared with other methods. Furthermore the oxidation can be performed at low temperatures, where other procedures fail.

Other oxygen donors such as peroxides and sodium hypochlorite in combination with Fe(tpp)Cl or Mn(tpp)Cl are also able to oxidize nitrosobenzene to nitrobenzene, but the reaction is not as fast as that with iodosylbenzene. Furthermore, Fe(tpp)Cl acts as a better catalyst than Mn(tpp)Cl.

‡ The reactions were followed by g.l.c. (methylsilicone). The conditions were adjusted for every experiment. After a reaction had finished the mixture was separated by column chromatography. The products were then checked by m.p. and mass spectrometry.

In the oxidation of nitroso compounds catalysed by Fe(tpp)Cl with iodosylbenzene as oxygen donor the first step is formation of an oxo-iron porphyrin complex which acts as the active catalyst. The structure of the active catalyst is usually represented as shown in (1).^{1,2} However this structure has recently been questioned, from both experimental⁶ and theoretical⁷ points of view, and structure (2) has been suggested as an alternative, in which the oxygen is inserted into one of the iron-nitrogen bonds. With (2) as model for the oxo-iron porphyrin, the mechanism for the oxidation of the nitroso to the nitro group might be formulated as shown in Scheme 1.

It is conceivable that another mechanism operates when hydrogen peroxide is used as oxygen donor.⁸

A detailed investigation of this reaction and of its mechanism is under way.

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