

## Iron(III) Porphyrin promoted Aerobic Oxidation of Sulphur Dioxide

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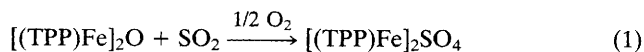
In the presence of sulphur dioxide and oxygen gas, the oxo-bridged tetraphenylporphyrinatoiron(III) dinuclear complex has been converted to the corresponding sulphato-bridged iron(III) complex.

Oxidation of SO<sub>2</sub> to sulphur(VI) species is of current industrial and environmental interest. Oxo- or dioxo-metal complexes may serve as effective catalysts for air oxidation of SO<sub>2</sub>,<sup>1</sup> *e.g.*, V<sub>2</sub>O<sub>5</sub> is utilized at temperatures above 400 °C for H<sub>2</sub>SO<sub>4</sub> production by the contact process.<sup>2</sup> A great many stoichiometric oxidations are also known in which co-ordinated SO<sub>2</sub> is air oxidized, or in which gaseous SO<sub>2</sub> is oxidized by a metal-dioxygen complex.<sup>3</sup>

Valentine and co-workers have recently shown that metalloporphyrin peroxo complexes react with SO<sub>2</sub> to give the sulphato complexes.<sup>4</sup> The dinuclear  $\mu$ -peroxo(tetraphenylporphyrinato)iron(III), (TPP)Fe–O–O–Fe(TPP), species which is thermally stable only at –80 °C,<sup>5</sup> reacts with SO<sub>2</sub> to produce the  $\mu$ -sulphato complex, [(TPP)Fe]<sub>2</sub>(SO<sub>4</sub>). The mononuclear peroxoiron(III) complex, (TPP)FeO<sub>2</sub><sup>–</sup>, and the

peroxotitanium(IV) complex, (TPP)TiO<sub>2</sub>, also react with SO<sub>2</sub> to give the corresponding sulphato complexes.<sup>4</sup>

It is perhaps not surprising that the peroxoiron(III) porphyrin complexes show reactivity that parallels other peroxy derivatives in oxidation of SO<sub>2</sub> to sulphate ion. However, we have found that the common  $\mu$ -oxoiron(III) species, [(TPP)Fe]<sub>2</sub>O, also reacts with SO<sub>2</sub> in the presence of O<sub>2</sub> to give the  $\mu$ -sulphatoiron(III) complex [equation (1)].



The SO<sub>2</sub> oxidation reactions typically were carried out in septum-sealed NMR tubes. The SO<sub>2</sub> gas (Aldrich, 99.9+%) was gently bubbled into a CD<sub>2</sub>Cl<sub>2</sub> solution of [(TPP)Fe]<sub>2</sub>O (2 mM) for 5 min. Under anaerobic conditions this treatment

induces no change in the optical spectrum at ambient temperature, and no change in the  $^1\text{H}$  NMR spectra at either ambient or dry ice temperatures. This observation is consistent with a recent report of the low reactivity of  $[(\text{TPP})\text{Fe}]_2\text{O}$  with  $\text{SO}_2$  under anaerobic conditions.<sup>6</sup> However, when excess dry oxygen is introduced into the NMR tube at room temperature, the proton NMR signal at  $\delta$  13.5 (pyrrole) for the antiferromagnetically coupled  $[(\text{TPP})\text{Fe}]_2\text{O}$  is shifted to  $\delta$  71.5. Likewise, bands in the optical spectra, at 407, 572, and 612 nm for  $[(\text{TPP})\text{Fe}]_2\text{O}$ , were replaced by bands at 348, 372, 407, 508, 576, and 680 nm. The optical and NMR spectra of the  $\text{SO}_2/\text{O}_2$  reaction product are identical with those of the previously characterized  $\mu$ -sulphatoiron(III) complex,  $[(\text{TPP})\text{Fe}]_2(\text{SO}_4)$ .<sup>7,8</sup>

Light is not required for promotion of  $\text{SO}_2$  oxidation by  $[(\text{TPP})\text{Fe}]_2\text{O}$  and there is no indication of porphyrin ring modification during the reaction. The monomeric chloro complex  $(\text{TPP})\text{FeCl}$ , does not serve to promote oxidation of  $\text{SO}_2$  in the presence of  $\text{O}_2$ . The sulphato complex is produced in the presence of  $[(\text{TPP})\text{Fe}]_2\text{O}$ ,  $\text{SO}_2$ ,  $\text{O}_2$ , and  $\text{CO}$ , and no iron(II) carbon monoxide complex is detected in the reaction mixture by proton NMR spectroscopy. If the reaction sequence required generation of porphyrinatoiron(II) with subsequent reaction by  $\text{O}_2$  to yield a peroxide intermediate, the presence of carbon monoxide would be expected to quench the reaction through formation of the stable  $\text{CO}$  complex.

To evaluate the possibility for involvement of the sulphito complex,  $[(\text{TPP})\text{Fe}]_2(\text{SO}_3)$ , an effort was made to generate this previously unreported derivative. Anaerobic addition of tetrabutylammonium sulphite (1.0 equiv.)<sup>9</sup> to a  $\text{CD}_2\text{Cl}_2$  solution of  $(\text{TPP})\text{Fe}(\text{SO}_3\text{CF}_3)$  is associated with the appearance of a unique pyrrole  $^1\text{H}$  NMR signal at  $\delta$  70.4. The trifluoromethanesulphonate anion,  $\text{SO}_3\text{CF}_3^-$ , is a very weak ligand that presumably can be replaced by sulphite ion, and accordingly the signal at  $\delta$  70.4 is tentatively assigned to

pyrrole resonance for the sulphito complex. There was no immediate conversion of this complex to the sulphate complex upon exposure of the solution to dry oxygen.

Acid-base reactions between  $\text{SO}_2$  and metal oxide groups are certainly anticipated. However, if any direct interaction occurs between  $\text{SO}_2$  and  $[(\text{TPP})\text{Fe}]_2\text{O}$ , the equilibrium constant must be very small, given the lack of spectral change for such a mixture. In this regard, direct  $\text{SO}_2$  interaction with the bridging oxo group or the vacant iron(III) co-ordination site would be expected to perturb the antiferromagnetic coupling, and hence the hyperfine NMR chemical shift value. Nonetheless, the possibility remains for weak association of  $\text{SO}_2$  and the  $\mu$ -oxoiron(III) unit with subsequent activation for oxidation by  $\text{O}_2$ .

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