# 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 $SO_2$ 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 $SO_2$,[1] *e.g.*, $V_2O_5$ is utilized at temperatures above 400 °C for $H_2SO_4$ production by the contact process.[2] A great many stoicheiometric oxidations are also known in which co-ordinated $SO_2$ is air oxidized, or in which gaseous $SO_2$ is oxidized by a metal–dioxygen complex.[3]

Valentine and co-workers have recently shown that metalloporphyrin peroxo complexes react with $SO_2$ to give the sulphato complexes.[4] The dinuclear μ-peroxo(tetraphenylporphyrinato)iron(III), (TPP)Fe–O–O–Fe(TPP), species which is thermally stable only at −80 °C,[5] reacts with $SO_2$ to produce the μ-sulphato complex, $[(TPP)Fe]_2(SO_4)$. The mononuclear peroxoiron(III) complex, $(TPP)FeO_2^-$, and the peroxotitanium(IV) complex, $(TPP)TiO_2$, also react with $SO_2$ to give the corresponding sulphato complexes.[4]

It is perhaps not surprising that the peroxoiron(III) porphyrin complexes show reactivity that parallels other peroxy derivatives in oxidation of $SO_2$ to sulphate ion. However, we have found that the common μ-oxoiron(III) species, $[(TPP)Fe]_2O$, also reacts with $SO_2$ in the presence of $O_2$ to give the μ-sulphatoiron(III) complex [equation (1)].

$$[(TPP)Fe]_2O + SO_2 \xrightarrow{1/2\ O_2} [(TPP)Fe]_2SO_4 \qquad (1)$$

The $SO_2$ oxidation reactions typically were carried out in septum-sealed NMR tubes. The $SO_2$ gas (Aldrich, 99.9+%) was gently bubbled into a $CD_2Cl_2$ solution of $[(TPP)Fe]_2O$ (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 $^1$H NMR spectra at either ambient or dry ice temperatures. This observation is consistent with a recent report of the low reactivity of $[(TPP)Fe]_2O$ with $SO_2$ under anaerobic conditions.[6] However, when excess dry oxygen is introduced into the NMR tube at room temperature, the proton NMR signal at δ 13.5 (pyrrole) for the antiferromagnetically coupled $[(TPP)Fe]_2O$ is shifted to δ 71.5. Likewise, bands in the optical spectra, at 407, 572, and 612 nm for $[(TPPFe)]_2O$, were replaced by bands at 348, 372, 407, 508, 576, and 680 nm. The optical and NMR spectra of the $SO_2/O_2$ reaction product are identical with those of the previously characterized μ-sulphatoiron(III) complex, $[(TPP)Fe]_2(SO_4)$.[7,8]

Light is not required for promotion of $SO_2$ oxidation by $[(TPP)Fe]_2O$ and there is no indication of porphyrin ring modification during the reaction. The monomeric chloro complex (TPP)FeCl, does not serve to promote oxidation of $SO_2$ in the presence of $O_2$. The sulphato complex is produced in the presence of $[(TPP)Fe]_2O$, $SO_2$, $O_2$, and 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 porphinatoiron(II) with subsequent reaction by $O_2$ to yield a peroxide intermediate, the presence of carbon monoxide would be expected to quench the reaction through formation of the stable CO complex.

To evaluate the possibility for involvement of the sulphito complex, $[(TPP)Fe]_2(SO_3)$, an effort was made to generate this previously unreported derivative. Anaerobic addition of tetrabutylammonium sulphite (1.0 equiv.)[9] to a $CD_2Cl_2$ solution of $(TPP)Fe(SO_3CF_3)$ is associated with the appearance of a unique pyrrole $^1$H NMR signal at δ 70.4. The trifluoromethanesulphonate anion, $SO_3CF_3^-$, is a very weak ligand that presumably can be replaced by sulphite ion, and accordingly the signal at δ 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 $SO_2$ and metal oxide groups are certainly anticipated. However, if any direct interaction occurs between $SO_2$ and $[(TPP)Fe]_2O$, the equilibrium constant must be very small, given the lack of spectral change for such a mixture. In this regard, direct $SO_2$ interation 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 $SO_2$ and the μ-oxoiron(III) unit with subsequent activation for oxidation by $O_2$.

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