

Photoassisted Electron Transfer Between Sulfur Dioxide and Tin(IV) Phthalocyanines

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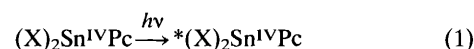
Photolysis of tin(IV) phthalocyanine complexes in the presence of sulfur dioxide shows a first-order kinetic dependence on sulfur dioxide, and a one-electron reduction of SnPc to an anion radical species.

Oxidation of sulfur dioxide to sulfur(VI) species is of current industrial and environmental interest. Metalloporphyrin complexes are known to react with SO₂ to give sulfonato metalloporphyrin complexes.¹⁻³ Interactions of SO₂ with iron (FePc) and cobalt (CoPc) phthalocyanine complexes have been reported.⁴ These complexes show electrocatalytic activity towards oxidation of SO₂ in acid media. However, no photochemical and mechanistic studies have been reported for the oxidation of SO₂ by metallophthalocyanine complexes. The use of solar energy as a driving force for the oxidation of SO₂ is of interest.

Experiments for the photochemical reduction of tin(IV) phthalocyanine complexes, SnPc(OH)₂ and SnPcCl₂, in the presence of sulfur dioxide, were performed by adding SO₂, dissolved in pyridine, to pyridine solutions of the SnPc complexes. There was no spectroscopic evidence for the displacement of the axial OH⁻ and Cl⁻ in SnPc(OH)₂ and SnPcCl₂, by pyridine. The solutions containing SnPc complexes and SO₂ were deaerated and then photolysed with a 50 W tungsten lamp. Fig. 1 shows the electronic absorption spectral changes observed during the photolysis. The Q band observed at 696 nm for the SnPc complexes is reduced in intensity and two new (weaker) bands are formed at 585 and

616 nm. These spectral changes are typical of ring reduction in metallophthalocyanine complexes,⁵ the new bands at 585 and 616 nm are characteristic of [Sn^{IV}Pc(-3)(OH)₂]⁻ (Pc²⁻ = phthalocyanine dianion) anion radical species.⁶ Exposure of the photoreduced species to air, resulted in the complete regeneration of the original Sn^{IV}Pc²⁻ species. The spectra gave no evidence of the formation of aggregation products on photolysis.

The formation of the photoreduced species was found to be first order in both SnPc (Fig. 2) and SO₂ (Fig. 3). The first step in the photolysis is expected to be the photoexcitation of the SnPc species [eqn. (1)].^{6,7} This is then followed by the



interaction of the photoexcited ^{*}SnPc species with the SO₂ molecule with a subsequent electron transfer from the latter to the former [eqn. (2)]. It is likely that the SO₂ is coordinated to

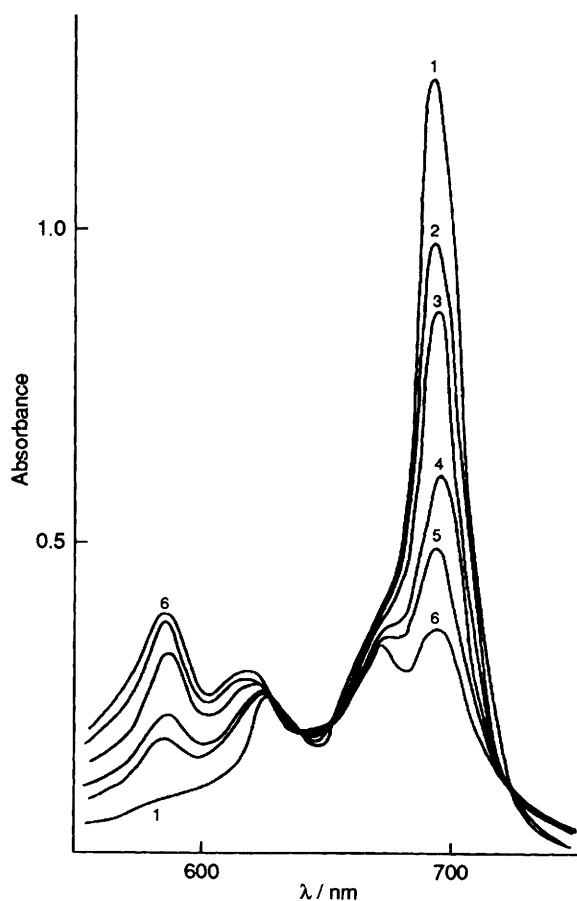
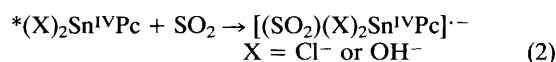


Fig. 1 Absorption spectral changes observed during the photolysis of SnPc(OH)₂ in pyridine, in the presence of 1.7 mol dm⁻³ sulfur dioxide (dissolved in pyridine). Photolysis times (1) 0 (2) 25 (3) 40 (4) 90 (5) 120 (6) 180 s.

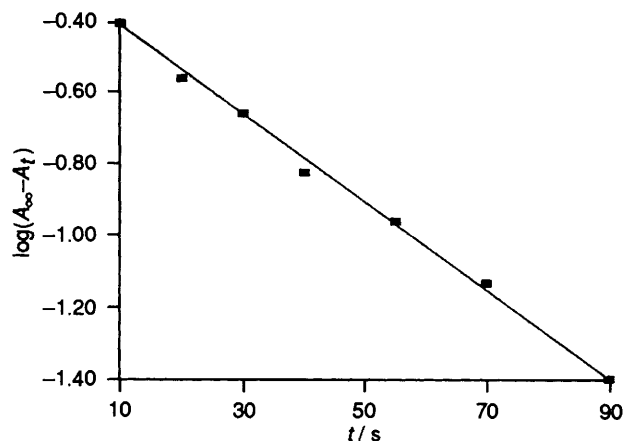


Fig. 2 Plot of t/s vs. $\log A$ for the photolysis of SnPc(OH)₂ in the presence of SO₂

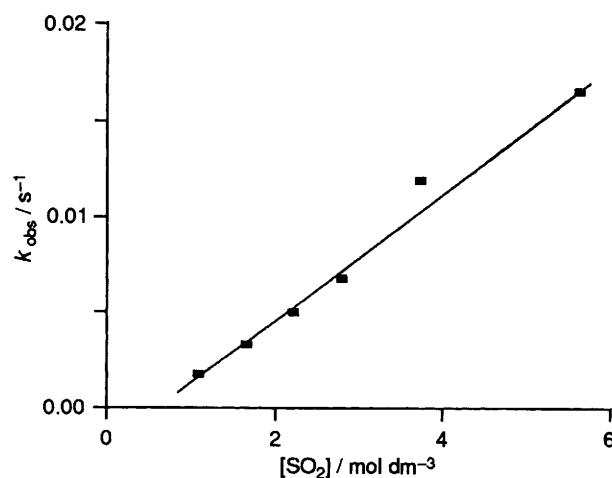


Fig. 3 Plot of k_{obs}/s^{-1} for SnPc(OH)₂ vs. $[\text{SO}_2]/\text{mol dm}^{-3}$

the metal centre during the electron transfer, as has been suggested for the electrocatalytic oxidation of SO₂ by CoPc and FePc.⁴

The reactive excited state following the photolysis of Sn^{IV}Pc is expected to be the ³ππ* state.⁷ This state is readily quenched by electron-transfer reactions in metallophthalocyanine complexes.

The fact that the reduction of Sn^{IV}Pc species by SO₂ could only occur in deaerated solutions, suggests that higher oxides of sulfur were not formed during the photolysis. The formation of such complexes is normally accompanied by dimerization in metalloporphyrin complexes. When solutions of the photoreduced Sn^{IV}Pc complexes were exposed to air and the solvent evaporated, a new IR band was observed at 610 cm⁻¹. This band is associated with the presence of free sulfate.

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