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 SO_2 to give sulfonato metalloporphyrin complexes.[1-3] Interactions of SO_2 with iron (FePc) and cobalt (CoPc) phthalocyanine complexes have been reported.[4] These complexes show electrocatalytic activity towards oxidation of SO_2 in acid media. However, no photochemical and mechanistic studies have been reported for the oxidation of SO_2 by metallophthalocyanine complexes. The use of solar energy as a driving force for the oxidation of SO_2 is of interest.

Experiments for the photochemical reduction of tin(IV) phthalocyanine complexes, $SnPc(OH)_2$ and $SnPcCl_2$, in the presence of sulfur dioxide, were performed by adding SO_2, 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 $SnPcCl_2$, by pyridine. The solutions containing SnPc complexes and SO_2 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 $[Sn^{IV}Pc(-3)(OH)_2]^{\cdot-}$ (Pc^{2-} = phthalocyanine dianion) anion radical species.[6] Exposure of the photoreduced species to air, resulted in the complete regeneration of the original $Sn^{IV}Pc^{2-}$ species. The spectra gave no evidence of the formation of aggregation products on photolysis.

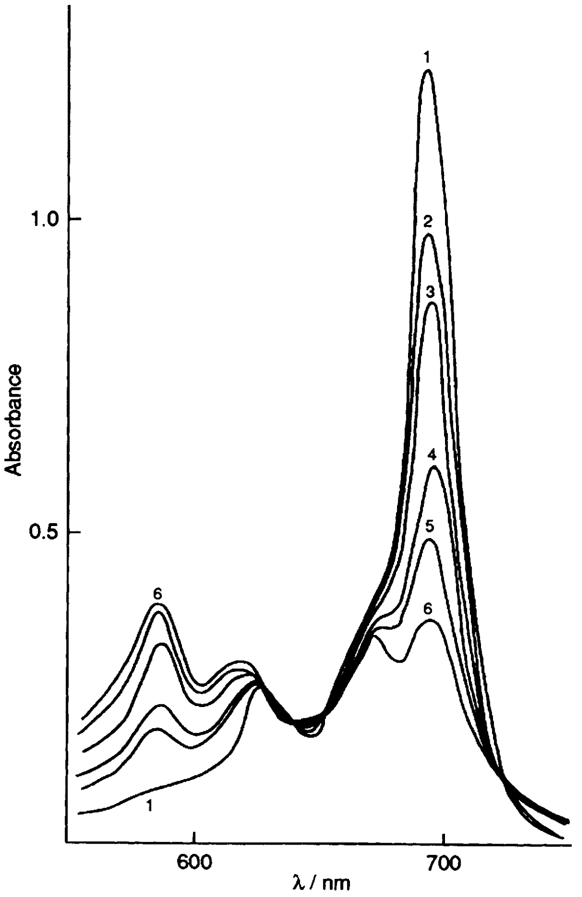

Fig. 1 Absorption spectral changes observed during the photolysis of $SnPc(OH)_2$ in pyridine, in the presence of 1.7 mol dm^{-3} sulfur dioxide (dissolved in pyridine). Photolysis times (1) 0 (2) 25 (3) 40 (4) 90 (5) 120 (6) 180 s.

The formation of the photoreduced species was found to be first order in both SnPc (Fig. 2) and SO_2 (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

$$(X)_2Sn^{IV}Pc \xrightarrow{h\nu} {}^*(X)_2Sn^{IV}Pc \qquad (1)$$

interaction of the photoexcited *SnPc species with the SO_2 molecule with a subsequent electron transfer from the latter to the former [eqn. (2)]. It is likely that the SO_2 is coordinated to

$$^*(X)_2Sn^{IV}Pc + SO_2 \rightarrow [(SO_2)(X)_2Sn^{IV}Pc]^{\cdot-}$$
$$X = Cl^- \text{ or } OH^- \qquad (2)$$

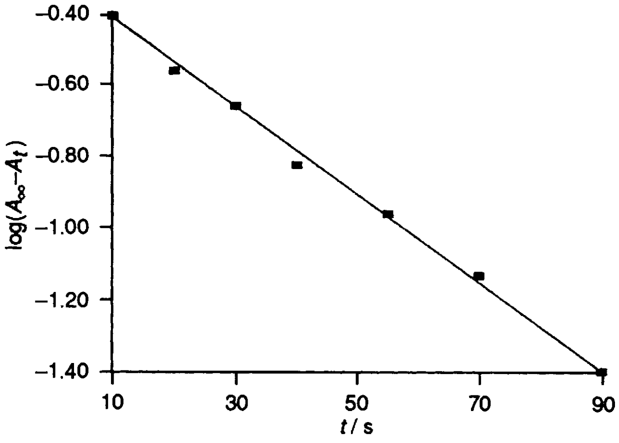

Fig. 2 Plot of t/s vs. log A for the photolysis of $SnPc(OH)_2$ in the presence of SO_2

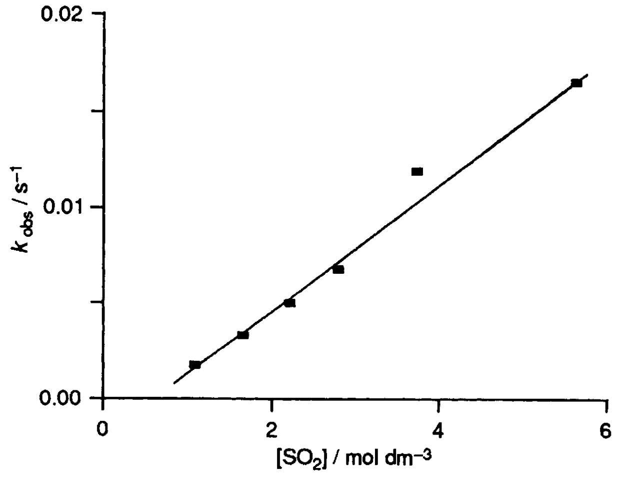

Fig. 3 Plot of k_{obs}/s^{-1} for $SnPc(OH)_2$ vs. $[SO_2]$/mol dm^{-3}

the metal centre during the electron transfer, as has been suggested for the electrocatalytic oxidation of SO_2 by CoPc and FePc.[4]

The reactive excited state following the photolysis of Sn^{IV} Pc is expected to be the $^3\pi\pi^*$ 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 SO_2 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 metalloporhyrin 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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