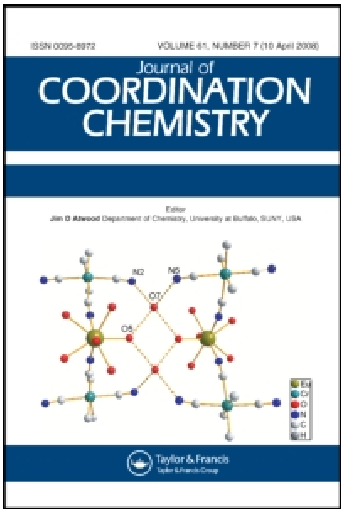

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PHOTO-ASSISTED ELECTRON TRANSFER IN A NICKEL(II) PORPHYRIN COMPLEX: FORMATION OF NICKEL(III)-PORPHYRIN π-CATION RADICAL

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Note

PHOTO-ASSISTED ELECTRON TRANSFER IN A NICKEL(II) PORPHYRIN COMPLEX: FORMATION OF NICKEL(II)-PORPHYRIN π-CATION RADICAL

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In sunlight the complex $Ni^{II}(TPP)$ {TPP = tetraphenylporphyrin} undergoes photolysis in CH_2Cl_2 to produce a stable nickel porphyrin π-cation radical $[Ni^{II}TPP^{\bullet}]^+$ species which has been characterised by epr measurement.

Keywords: Nickel(II); porphyrin; photochemistry; electrochemistry

INTRODUCTION

Nickel porphyrin complexes[1–5] have long attracted attention, owing to their possible relevance to biological systems. Of particular interest is the reversible intramolecular electron-transfer analogous to that proposed to occur in cytochromes.[6] Dolphin and co-workers[7] reported that electrochemical oxidation of $Ni^{II}(TPP)$ in CH_2Cl_2 results in the formation of the nickel porphyrin π-cation radical ($[Ni^{II}(TPP)^{\bullet}]^+$) and π-dication radical ($[Ni^{II}(TPP)^{\bullet}]^{2+}$) species. Upon cooling at 77 K, the latter species converts to a Ni(III)-porphyrin complex. This reversible, temperature-dependent transformation

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is quite similar to that postulated for cytochromes.[6] In an attempt to observe the same phenomenon through a photochemical route we have undertaken the present work which describes the formation of a stable (both at room temperature and 77 K) nickel(II)-porphyrin π-cation radical species by photolysis of $Ni^{II}(TPP)$ in CH_2Cl_2 using sun-light as the sole light source. As far as we are aware, this is the first report of its kind.

EXPERIMENTAL

The $[Ni^{II}(TPP)]$ complex was prepared by interacting free TPP ligand with $Ni(OAC)_2$ in refluxing DMF as described earlier.[8] All other reagents were of A.R. grade. Absorption spectra were recorded on a Shimadzu 160 spectrophotometer. Cyclic voltammeteric studies were performed using a Princeton Applied Research (PAR 174A) electrochemical instrument. A platinum working electrode and a saturated calomel electrode (SCE) as reference was used for this purpose. Coulometric experiments at constant potential were carried out with a PAR 173 potentiostat equipped with a PAR 179 current integrator. A coulometric cell of three-electrode configuration consisting of a platinum gauze working electrode, a platinum wire counter electrode separated from the main solution by a glass frit and an SCE as reference was used for this purpose. EPR spectra of photolysed solutions were recorded on a Bruker X-band (ESP 300) spectrometer (100 kHz field modulation) with a built-in ERO NMR gaussmeter (for magnetic field calibrations). The 'g' values were determined with DPPH ($g = 2.003$) as marker. Photolysis of $[Ni^{II}(TPP)]$ complex in $CH_2Cl_2(1 \times 10^{-4} M)$ was carried out in a quartz tube. The solution was exposed to sunlight. Spectroscopic changes during irradiation time were recorded at certain time intervals (15 min apart). Completion of photolysis was observed after 4 h with no further change in the spectrum being observed. For epr experiments a bulk solution ($500 cm^3$) of $Ni^{II}(TPP)$ was photolysed and concentrated prior to epr measurements.

RESULTS AND DISCUSSION

Upon irradiation (with sunlight), the solution of $[Ni^{II}(TPP)]$ in CH_2Cl_2 undergoes photolysis as seen by the changes shown in Figure 1. Spectroscopic change is characterised by the disappearance of the soret (418 nm)

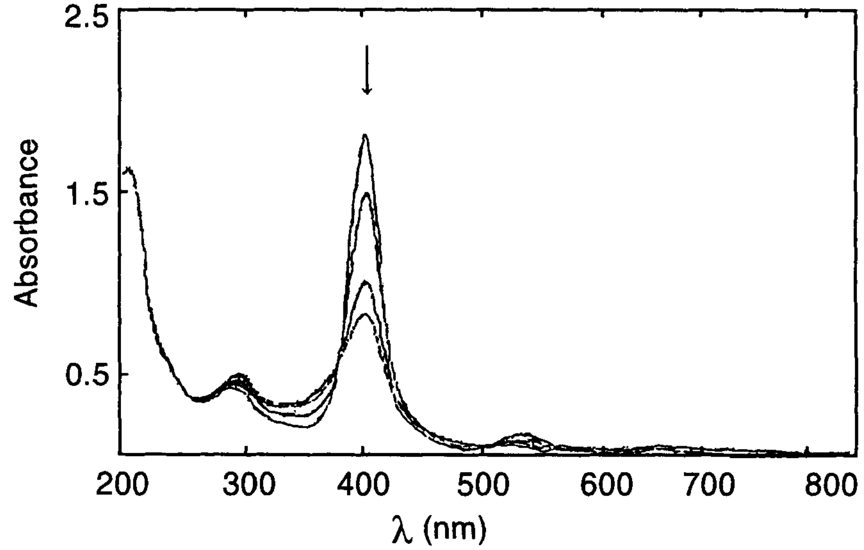

FIGURE 1 Spectroscopic changes associated with the formation of the $[Ni^{II}(TPP)^{\bullet}]^{+}$ π-cation radical in CH_2Cl_2. Spectra are recorded at 30 min intervals during photolysis.

and visible (526 nm) bands characteristic of filled π-orbitals of the porphyrin ligand (TPP). A similar change was reported by Dolphin *et al.*[7] for the formation of the π-cation radical species $[Ni^{II}(TPP)^{\bullet}]^{+}$ by the electrochemical oxidation of $[Ni^{II}(TPP)]$ (at 1.24 V) in CH_2Cl_2.

The EPR spectrum (at room temperature) of the photolysed solution of $Ni^{II}(TPP)$ shows features ($g = 2.008$ and $\Delta H = 14G$) quite similar to those reported[7] for Ni(II)-porphyrin π-cation radical species. No change in the spectrum was observed upon cooling to 77 K. It is important to note that the epr spectrum of the π-cation radical (formed by the oxidation of $Ni^{II}(TPP)$ at 1.24 V) at 77 K was not reported by Dolphin *et al.*[6] We carried out a few epr experiments on the electrolysed (at 1.24 V) solution of $Ni^{II}(TPP)$, both at room temperature and at 77 K and found that there is not much difference in spectroscopic features at both temperatures. Further, the temperature-dependent intramolecular electron-transfer was reported to occur only in the π-cation radical dication $[Ni(TPP)^{\bullet}]^{2+}$ (obtained by further oxidation of $[Ni^{II}(TPP)^{\bullet+}]^{+}$ at 1.44 V) which at 77 K converts to a $Ni^{III}(TPP)^{+}$ species. Based on the above experimental facts and considering the earlier observations[7] it is suggested that exposure to sunlight of $[Ni^{II}(TPP)]$ in CH_2Cl_2 results in the formation of a stable

π-cation radical species $[\mathrm{Ni^{II}(TPP)^\bullet}]^+$ through the following pathway.

$$\mathrm{CH_2Cl_2} \xrightarrow{h\nu} \mathrm{CH_2Cl^\bullet + Cl^\bullet} \tag{1}$$

$$[\mathrm{Ni^{II}(TPP)}] + \mathrm{Cl^\bullet} \longrightarrow [\mathrm{Ni^{II}(TPP)^\bullet}]^+ + \mathrm{Cl^-} \tag{2}$$

$$[\mathrm{Ni^{II}(TPP)}] + \mathrm{Cl^\bullet} \longrightarrow [\mathrm{Ni^{III}(TPP)}]^+ + \mathrm{Cl^-} \tag{3}$$

$$[\mathrm{Ni^{III}(TPP)}]^+ \longrightarrow [\mathrm{Ni^{II}(TPP)^\bullet}]^+ \tag{4}$$

During photolysis, a chloride radical ($\mathrm{Cl^\bullet}$) is produced[9] in the reaction mixture. This $\mathrm{Cl^\bullet}$ is very active and reacts with $\mathrm{Ni^{II}(TPP)}$ to produce the $[\mathrm{Ni^{II}(TPP)^\bullet}]^+$ π-cation radical species. However, it could not be distinguished whether Cl directly oxidise the filled π-orbitals of coordinated porphylin (TPP) ligand or the metal centre followed by rapid intramolecular electron transfer from a π-orbital to nickel(III) to yeild $[\mathrm{Ni^{II}(TPP)^\bullet}]^+$ (3 and 4). Stabilisation of π-cation radical species formed in the reaction mixture is envisaged through the axial coordination of $\mathrm{Cl^-}$, which is well documented in the case of $[\mathrm{Zn(TPP)^\bullet}]^+$.[10]

In conclusion, the present work clearly shows a photochemical route for oxidation of [Ni(TPP)]. Further studies with other macrocyclic complexes of nickel(II) are in progress to address the intriguing features of this important electron transfer process.

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