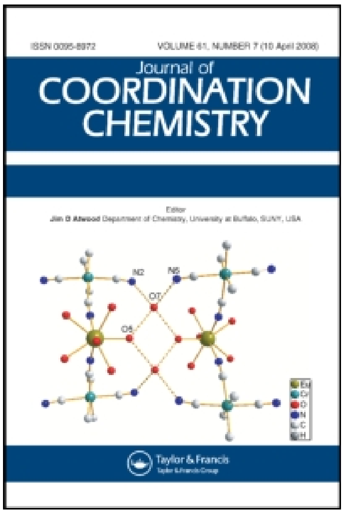

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Photochemical cleavage of nitrate ion coordinated to a Cr(III) porphyrin

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Photochemical cleavage of nitrate ion coordinated to a Cr(III) porphyrin#

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Photolysis of the nitrato chromium(III) tetraphenylporphyrinato compound Cr(TPP)(NO_3) (TPP, tetraphenylporphyrin) in toluene solution clearly leads to the formation of the Cr(IV) oxo complex Cr(TPP)(O) with a quantum yield of 0.011. The other product, NO_2, was detected quantitatively by its reaction with the spin trapping agent 2,2,6,6-tetramethyl-piperidine-1-oxyl.

Keywords: Chromium(III); Photochemistry; Nitrite; Nitrogen dioxide

1. Introduction

There is considerable interest in the chemistry of nitrogen oxides inspired by the now well-established physiology of nitric oxide (NO) [1] and the growing body of knowledge demonstrating that other NO_x species are very relevant to mammalian biochemistry [2]. In this context, our laboratory [3] and others [4] have been concerned with developing photochemical methods for the delivery of NO to specific tissues for potential therapeutic purposes, for example as a radiation sensitizer [5]. In general, the goal would be to utilize a compound that is biologically inactive, unless excited by the appropriate wavelength of light, at which point NO would be released. Among the compounds studied are metal nitrosyl complexes with direct M–NO bonds that are photoactive and metal nitrito complexes M–ONO for which photochemical β-cleavage of the MO–NO bond leads to NO release. During the course of such investigations, the question arose whether one could design compounds that are photoactive for the release of nitrogen dioxide as well, given that NO_2 is also biologically relevant, although primarily *via* deleterious effects [6]. The photolysis of the nitrate ion complex Cr(TPP)(ONO_2) (TPP, tetraphenylporphyrin) (**1**, TPP^{2-} = *meso*-tetraphenylporphyrinato dianion) leading to β-cleavage of the $Cr^{III}O–NO_2$ bond as

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#This article has been submitted to honor the distinguished career of Prof. Rudi van Eldik.

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shown in equation (1) is described here. The quantitative evaluation of the NO_2 released is also reported.

$$Cr^{III}(TPP)(ONO_2) \xrightarrow{h\nu} Cr^{IV}(TPP)(O) + NO_2 \qquad (1)$$

Inspiration for this study was drawn in part from the demonstration by Yamaji *et al.* [7] that irradiation of the Cr(III) nitrito complex Cr(TPP)(ONO) in degassed benzene resulted in labilization of NO to give Cr^{IV}(TPP)(O). This contrasts with the analogous photochemistry of Mn^{III}(TPP)(ONO), which results in homolytic Mn^{III}–ONO bond cleavage to give principally Mn^{II}(TPP) as an intermediate [8], and one might suggest that the facility of equation (1) is favored by the greater oxophilicity of the chromium center. It was later demonstrated in this laboratory that *trans*-$[Cr(cyclam)(ONO)_2][X]$ (cyclam = 1,4,8,11-tetraazacyclotetra-decane) undergoes similar β-cleavage of the CrO–NO bond in aqueous solution [9]. This reaction is being exploited with $Cr(cyclam)(ONO)_2^+$ and other Cr(III) complexes with various chromophore pendants to the cyclam ligand as a photochemical methodology for the delivery of the bioregulatory molecule NO to biological targets [10]. In this context, it was reasoned that a chromium(III) *nitrato* complex would be well-suited for analogous NO_2 generation *via* β-bond cleavage of the O-bound ligand.

There are indeed several precedents to the photoreaction described by equation (1). Suslick and Watson [11] reported that photolysis of $Mn^{III}(TPP)(NO_3)$ produces the high-valent metal–oxo species Mn^{IV}(TPP)(O) by homolytic cleavage of the MnO–NO_2 bond but concluded that photolysis of the $Fe^{III}(TPP)(NO_3)$ occurs by heterolytic cleavage to give a highly reactive Fe^V(TPP)(O) intermediate. Newcomb *et al.* [12] also demonstrated photo-induced β-bond homolytic MO–NO_2 cleavage for $Fe^{IV}(Ar_3C)(ONO_2)$ (Ar_3C^{3-} = 5,10,15-tris(pentafluoro-phenyl)corrolate) formed transiently by the reaction of $Fe^{IV}(Ar_3C)Cl$ with $AgNO_3$. Flash photolysis resulted in the formation of Fe^V(corrole)(O). In neither study was the fate of the nitrogen intermediates well-characterized. Photochemical nitrate cleavage was also reported by Kunkely and Vogler [13], who found that 254 nm photolysis of $Cu^I(PPh_3)_2(NO_3)$ gives Cu(II), Ph_3PO, and NO, presumably *via* the intermediacy of $Cu^{II}O$ and NO_2. Similarly, Cheng and Bakac [14] recently described the 266 nm flash photolysis of $Cr(H_2O)_5(NO_3)^{2+}$ in the presence of halide ions and reported that the CrO^{2+} ion was generated and it participates in a variety of redox reactions with solution components. A small absorbance increase at 260–270 nm was attributed to concomitant NO_2 formation.

2. Experimental

2.1. *Materials*

Spectrochemical grade toluene (Fisher) was prepared by washing with sulfuric acid and neutralizing with NaOH to remove residual thiophene, followed by distillation from sodium. Cr(TPP)Cl (Strem Chemicals), silver nitrate (Sigma), and all additional solvents were of reagent grade or higher and used without purification.

The synthesis of $Cr(TPP)(ONO_2)$ (**1**) was accomplished by stirring a biphasic mixture of Cr(TPP)Cl in dichloromethane and a saturated aqueous $AgNO_3$ solution overnight.

The organic layer was separated and then the solvent was removed under reduced pressure. The resulting solid was then redissolved in warm dry toluene and filtered through Celite to remove residual silver salt solids. Toluene was removed by rotary evaporation under reduced pressure, resulting in a dark green solid in 46% yield. The solid was stored in the glovebox until use. The UV-Vis spectrum of **1** in toluene displays the Soret band with λ_{max} at 448 nm, ($\varepsilon = (1.65 \pm 0.15) \times 10^5$ (mol $L^{-1})^{-1}$ cm^{-1}), Q bands at 564 ($(8.9 \pm 0.2) \times 10^3$) and 602 nm ($(7.6 \pm 0.1) \times 10^3$). This spectrum is very similar to those of the respective chloro and nitrito analogs Cr(TPP)(Cl) and Cr(TPP)(ONO) [7]. The IR spectrum of **1** (KBr) shows three bands at 1342, 1488, and 1532 cm^{-1}, characteristic of an η^1–O coordinated nitrate ligand [15]. Analysis (NuMega Labs, San Diego, CA, USA): Calcd: $(C_{44}H_{28}N_4)Cr(ONO_2) \cdot H_2O$: C, 70.96; H, 4.06; and N, 9.40. Found (average of two): 69.42; H, 4.90; and N, 9.15.

2.2. *Instruments*

All electronic spectra were recorded using a Hewlett Packard model HP8452A diode array spectrophotometer with 2 nm resolution. Spectra were obtained using a 1 cm quartz cuvette. IR spectra were recorded with a Bio-Rad FTS-60 SPC 3200 FTIR spectrophotometer. Solid state measurements were made as KBr pellets and solution measurements were made through a 0.2 mm CaF_2 cell. All spectra were acquired as 16 scans from 400 to 4000 cm^{-1} with a 2 cm^{-1} resolution against an air background. Electron paramagnetic resonance spectra were recorded on a Bruker Biospin EMX spectrometer operating at 9.8 GHz using the stable free radical 2,2-diphenyl-1-picrylhydrzyl with a g value of 2.0037 as a standard.

2.3. *Photochemical studies*

Quantum yields for the photoreaction in equation (1) were determined spectroscopically by monitoring the disappearance of **1** (448 nm) for solutions of **1** in toluene using a high pressure mercury lamp as the continuous photolysis source and a 366 nm interference filter for wavelength selection. Light intensities were determined by ferrioxalate actinometry [16].

3. Results and discussion

Irradiation of a deaerated toluene solution of $Cr(TPP)(ONO_2)$ (4×10^{-6} mol L^{-1}) at 366 nm resulted in disappearance of the UV-Vis absorption bands characteristic of **1**. These changes coincided with the appearance of bands characteristic of a different porphyrin species with $\lambda_{Soret} = 432$ and $\lambda_Q = 544$ nm (figure 1). Clean isosbestic points were observed at 408, 442, and 556 nm indicating that there are no spectrally observable secondary photoreactions of the Cr photoproducts. The quantum yield for disappearance of **1** (Φ_d) was measured to be 0.011 ± 0.001 mol per Einstein.

Attempts to probe this reaction by flash photolysis kinetics ($\lambda_{irr} = 355$ nm) showed only an immediate bleach at 448 nm and an immediate absorbance increase at 432 nm,

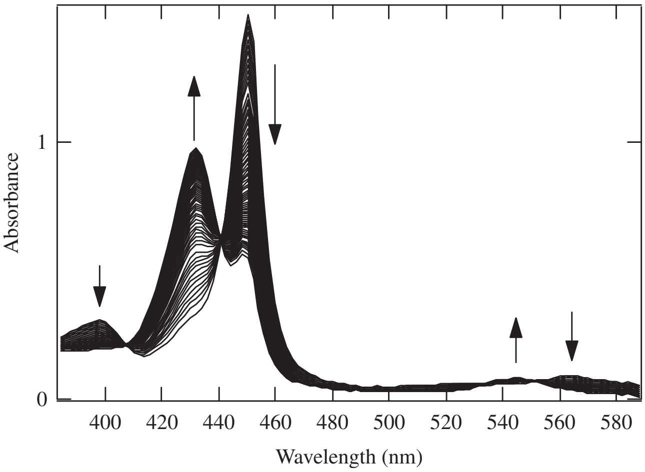

Figure 1. UV-Vis spectra changes resulting from the 366 nm photolysis of Cr(TPP)(ONO_2) (4×10^{-6} mol L^{-1}) in dry deaerated toluene.

thus the photoreaction appears to be over within the lifetime of the laser flash (15 ns) and there is no back reaction.

Comparison of the UV-Vis spectrum of the photochemical product that is formed after exhaustive photolysis of **1** matches that of the Cr(IV) oxo complex Cr(TPP)(O) (**2**) (λ_{max} (ε in $(mol\,L^{-1})^{-1}\,cm^{-1}$): 432 ($1.66 \times 10^5$ $(mol\,L^{-1})^{-1}\,cm^{-1}$) and 544 nm ($1.95 \times 10^4$)) reported previously and prepared in this laboratory by the published method [17]. Notably, there was no residual 448 nm peak; thus the sample contained no Cr(TPP)Cl, which is not photoactive under these conditions. Furthermore, the proton NMR, $ESMS^+$, and FTIR (KBr) spectra of the photoproduct matched closely those of authentic **2**. Preliminary photochemical experiments have been conducted with the analogous Cr(OEP)(ONO_2) complex (OEP^{2-} = octaethylporphyrinato dianion) and the results reveal similar photoreactivity, but with a lower quantum efficiency.

Based on these spectroscopic measurements, we conclude that the 366 nm photolysis of toluene solutions of **1** results in β-bond cleavage of the CrO–NO_2 bond to form Cr(TPP)(O) as shown in equation (1). This behavior is analogous to the previously reported photochemical β-bond cleavage of the CrO–NO linkages of Cr(III) nitrito complexes of porphyrinato and cyclam ligand systems [9, 10] and parallels the photochemistry of several M(ONO_2) complexes described in section 1 [11–14].

Tracing the end destination of the NO_2 generated by photolysis of Cr(TPP)(ONO_2) has proved elusive owing to the small amounts of NO_2 formed. Toluene nitration by NO_2 is a known reaction; however, various attempts to isolate and identify NO_2 modified toluene products by IR or NMR spectroscopy were unsuccessful. This was presumably due to the relatively small initial concentrations of **1** in the initial solutions, therefore also of any putative photolysis products. In order to address this issue, a much more sensitive experiment was carried using the stable free radical 2,2,6,6-tetramethyl-piperidine-1-oxyl (TEMPO), which is readily detected by EPR spectrometry. The EPR spectra of TEMPO were measured in several known

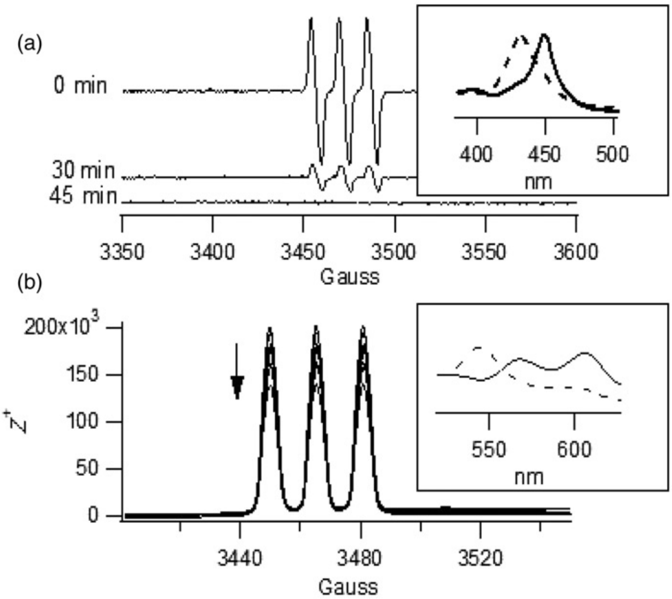

Figure 2. (a) Broad band photolysis of a deaerated toluene solution of Cr(TPP)(ONO$_2$) (1.7×10^{-5} mol L^{-1}) and TEMPO (initially 1.6×10^{-5} mol L^{-1}). The inset shows the complete conversion of **1–2** while the EPR spectrum shows complete depletion of the TEMPO signal. (b) The integrated EPR signal of a deaerated toluene solution of TEMPO (initially 2.66×10^{-4} mol L^{-1}) during broad band photolysis of **1** (initially 1.37×10^{-4} mol L^{-1}) over 45 min. The spectrum shown in the inset shows a decrease in the concentration of **1** by 0.80×10^{-4} mol L^{-1} in agreement with the final EPR signal (139 Z$^+$), which shows a decrease in the TEMPO concentration of 0.81×10^{-4} mol L^{-1}.

concentrations, and a calibration curve was obtained by plotting the integrated signal *versus* TEMPO. Efficient trapping of NO$_2$ by TEMPO has been demonstrated previously by Goldstein *et al.* [18]. Figure 2 illustrates experiments involving the photolysis of **1** in deaerated toluene solutions containing TEMPO in a quartz tube. One of these experiments was conducted with excess **1**, (figure 2a) and the other with excess TEMPO (figure 2b).

For the first experiment with TEMPO, broad band photolysis of a toluene solution of Cr(TPP)(ONO$_2$) (initially 1.7×10^{-5} mol L^{-1}) with a Hanovia high pressure mercury lamp converted **1** completely to Cr^{IV}(TPP)(O) (see inset) and correspondingly resulted in the nearly complete depletion of the EPR signal for TEMPO (initially 1.6×10^{-5} mol L^{-1}). Since the Cr(IV) spectrum is unaffected by the presence of TEMPO, we can conclude that the TEMPO is trapping another radical, namely, nitrogen dioxide.

In the second experiment, photolysis of Cr(TPP)(ONO$_2$) (initially 1.37×10^{-4} mol L^{-1}) led to partial depletion of the signal for TEMPO (initially 2.66×10^{-4} mol L^{-1}). According to the absorption spectra (figure 2b, inset), the change in concentration of **1** is -0.80×10^{-4} mol L^{-1}, while according to EPR spectra the change in the TEMPO concentration is -0.81×10^{-4} mol L^{-1} (as determined from independent calibration of the TEMPO signals). Thus, we conclude that the NO$_2$ generated by the photolysis of Cr(TPP)(ONO$_2$) is *quantitatively captured* by reaction with the stable TEMPO radical.

4. Summary

The continuous photolysis (366 nm) of the nitrato chromium(III) porphyrinate complexes Cr(TPP)(ONO_2) and Cr(OEP)(ONO_2) in toluene solutions results in β-bond cleavage of the CrO–NO_2 bond to give the corresponding oxo complex Cr^{IV}(TPP)(O) and Cr^{IV}(OEP)(O). The quantum yield for labilization of NO_2 from **1** is 0.011. The NO_2 product has been shown by EPR experiments to be trapped quantitatively in solution by the stable free radical TEMPO. This photochemical nitrate reductase reaction will serve as a model for the development of further chromium nitrate complexes that can be used as photochemical NO_2 precursors.

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