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Interaction of nitric oxide with cobalt(II) tetrasulfophthalocyanine

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Abstract

The interaction of nitric oxide (NO) with cobalt(II) tetrasulfophthalocyanine $[Co(II)TSPc]^{4-}$) has been studied. Coordination of NO is accompanied by electron transfer from the central metal in $[Co(II)TSPc]^{4-}$, the resulting complex being represented as $[(NO^{-})Co(III)TSPc]^{4-}$. The rate constant for the formation of this species is $k_f = 142 \pm 7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and an equilibrium constant of $3.0 \pm 0.5 \times 10^5 \text{ dm}^3 \text{ mol}^{-1}$ was obtained. When adsorbed to a glassy carbon electrode, $[Co(II)TSPc]^{4-}$ catalyses the oxidation and reduction of NO, with a detection limit of the order of 10^{-9} mol dm⁻³. Ammonia and hydroxylamine are some of the reduction products obtained for the reduction of NO on $[Co(II)TSPc]^{4-}$ -modified glassy carbon electrodes. ©2000 Elsevier Science Ltd All rights reserved.

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1. Introduction

Interest in the chemistry of nitric oxide (NO) has intensified in the last few years due to its importance in biological systems including neurotransmission, vascular dilation, cytotoxicity, immune response and regulation of blood pressure [1,2]. Excess concentrations of NO have been implicated as a major factor in a number of conditions, such as septic shock, and Parkinson's and Alzheimer's diseases [3,4]. There has been a surge of interest in the nature of coordination of NO to metalloporphyrins [4–13]. NO interacts with hemoglobin, myoglobin and cytochrome P450 forming NO compounds [14]. NO has a short half-life (depending on the concentration of oxygen) and has high reactivity with oxygen and hydrogen peroxide [1]. Current methods of detecting NO are indirect, relying on the measurement of secondary species such as nitrite and nitrate after removal from biological systems. Measurement of NO using bioassay, chemiluminescence and UV-Vis spectroscopy do not allow for in vivo detection, and require chemical pretreatment of the sample. Thus there is a growing interest in electrochemical sensors for analysis of NO in cells [15-18], based on its electrocatalytic oxidation. Nickel(II) and iron(II) porphyrin complexes and unmetallated porphyrin have been employed in modifying electrodes for the detection of NO [19-27]. The mechanism for the catalytic oxidation of NO by metallopor-

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phyrins is not well understood. For example, the Ni(III)/ Ni(II) couple has been implicated in NO determination using electrodes modified with nickel(II) porphyrin complexes [19,20], but other researchers have reported that the Ni(III)/ Ni(II) couple plays no role in the electrocatalytic oxidation of NO [25].

Metallophthalocyanine (MPc) complexes have been used successfully as electrocatalysts for many reactions [28–36]. There are only a few reports on the interaction between NO and MPc complexes [37–42]. The use of MPc complexes for the electrocatalytic reduction or oxidation of NO still needs to be explored. It has recently been suggested that $[CoTSPc]^{4-}$ bound to immobilized imidazole-modified silica gel can be used as a water-soluble NO sorbent that does not dimerize, and hence can be used for the removal of NO from flue gas streams [37]. The present study explores the electrocatalytic oxidation and reduction of NO on glassy carbon electrodes modified with cobalt(II) tetrasulfophthalocyanine ($[CoTSPc]^{4-}$; Fig. 1). We also report on the kinetics and equilibria for the interaction between NO and $[CoTSPc]^{4-}$.

2. Experimental

2.1. Materials

Cobalt(II) tetrasulfophthalocyanine (Na₄[Co(II)TSPc]) was synthesized and purified according to the method of

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Fig. 1. Molecular structure of cobalt(II) tetrasulfophthalocyanines.

Weber and Busch [43]. NO was prepared by adding saturated sodium nitrite dropwise to a 0.2 mol dm⁻³ solution of H₂SO₄ under nitrogen atmosphere. The NO produced was passed through a column containing solid KOH to remove higher oxides and then bubbled into nitrogen-saturated deionized water. NO solutions in water were prepared freshly before use and kept in glass flasks fitted with a rubber septum. NO concentration in water was determined using the method proposed by Ascenzi et al. [38] or calculated using the reported solubility of 2.2×10^{-3} mol dm⁻³ at 25°C and 1.00 atm [38]. Tetraethylammonium perchlorate (TEAP) was recrystallized from ethanol before use as an electrolyte. Dimethylformamine (DMF) was freshly distilled.

2.2. Electrochemical methods

Electrochemical data were collected with the Bio-Analytical Systems (BAS) model CV-50W voltammetric analyser. For cyclic voltammetry, a glassy carbon electrode (GCE; 3.0 mm diameter) was used as a working electrode and a platinum wire as an auxiliary electrode. The reference electrode was the Ag|AgCl (3 mol dm⁻³ KCl). Concentrations of Na₄[Co(II)TSPc] in water were in the 10⁻⁴ to 10⁻³ mol dm⁻³ range for cyclic voltammetry. Phosphate buffers pH 4 and 7 were employed for electrochemical experiments. In some experiments sodium sulfate (0.05 mol dm⁻³) was employed as an electrolyte. For non-aqueous solutions TEAP was employed as an electrolyte.

For electrocatalytic reactions, a glassy carbon electrode modified with Na₄[Co(II)TSPc] (CoTSPc-GCE) was employed as a working electrode. The glassy carbon was modified by anodic electrodeposition from a 10^{-3} mol dm⁻³ solution of [CoTSPc]⁴⁻ in DMF containing 0.1 mol dm⁻³ TEAP as an electrolyte, as reported before [44]. The deposition was carried out by scanning repetitively at 100 mV s⁻¹ between -0.2 and 1.0 V versus Ag|AgCl (non-aqueous). Prior to coating, the GCE was polished with alumina on a Buehler felt pad, followed by soaking in dilute nitric acid and rinsing in water, acetone and the solvent of interest. For bulk electrolysis, a two-compartment cell was employed, with a

platinum plate of area 2.2 cm² as counter electrode and an Ag|AgCl (3 mol dm⁻³ KCl) reference electrode. The GCE modified by electrodeposition was used as a working electrode for bulk electrolysis. A nitrogen atmosphere was maintained for all electrochemistry experiments. Concentrations of NO were of the order of 10^{-4} to 10^{-3} mol dm⁻³ for electrocatalytic studies. Yields of ammonia were determined by the Nessler method [45] and by monitoring the absorbance at 400 nm. Hydroxylamine was determined spectroscopically using the specific test described in the literature [9].

2.3. Kinetics and equilibria

Kinetic and equilibrium studies were run at 21.0 ± 0.5 °C and monitored with a Cary 1E UV-Vis spectrophotometer. We monitored the appearance of the spectra due to the product formed following the addition of NO to solutions of [Co-TSPc]⁴⁻ in water. Typically, a known volume of the aqueous solution of [CoTSPc]⁴⁻ was added to a cell of 1 cm pathlength and deaerated using nitrogen. Then a known volume of a deaerated aqueous solution of NO was added to the cell and the spectra monitored with time. Bubbling of nitrogen into the cell was continued while adding the NO solution. The cell was fitted with a stopper to avoid oxygen affecting the reaction. Concentrations of [CoTSPc]⁴⁻ were kept constant at 5.0×10^{-6} mol dm⁻³, whereas NO concentrations were varied from 1.4×10^{-5} to 5.6×10^{-5} mol dm⁻³. Concentrations of [CoTSPc]⁴⁻ in water were determined using the published extinction coefficient of $5.8 \times 10^4 \text{ mol}^{-1} \text{ dm}^3$ cm^{-1} [46]. Since the concentration of the NO was larger than that of [CoTSPc]⁴⁻ by a factor of at least 10, pseudofirst-order conditions were assumed for kinetic studies. Solid CoTSPc-NO was prepared by bubbling NO into aqueous solutions of [CoTSPc]⁴⁻ and allowing the solvent to evaporate.

IR spectra were recorded using a Perkin–Elmer Spectrum 2000 IR spectrophotometer.

3. Results and discussion

3.1. Interactions with NO

The electronic absorption spectral properties of [Co-TSPc]^{4–} are well known. Like other tetrasulfonated phthalocyanines, this species forms aggregates in aqueous solution. The electronic absorption spectrum is explained in terms of the monomer/dimer equilibrium. The lower energy band near 670 nm has been attributed to the monomeric species and the higher energy band near 620 to the dimeric species [46]. On coordination of molecules such as nitrite and histidine, the peak due to the monomer increases in intensity and shifts to longer wavelengths, whereas the peak due to the dimeric species decreases in intensity [47,48]. Fig. 2 shows spectral changes that were observed when NO was added to solutions



Fig. 2. Electronic absorption spectral changes observed on addition of NO $(3.5 \times 10^{-5} \text{ mol dm}^{-3})$ to aqueous solutions of $[\text{Co}(\text{II})\text{TSPc}]^{4-}$. (a) Spectra immediately after addition of NO; (b) spectra 30 min after addition of NO.

of [Co(II)TSPc]⁴⁻. The monomeric peak of [CoTSPc]⁴⁻ was observed at 659 nm before addition of NO (Fig. 2a). The spectrum is typical for $[CoTSPc]^{4-}$ in water, at low electrolyte concentrations; the peak due to the monomer dominates under these conditions [46]. On addition of NO to $[Co(II)TSPc]^{4-}$, a shift in the peak due to the monomer, from 659 to 667 nm, was observed. The intensity of the peak at 667 nm increased isosbestically with time (Fig. 2b). The shift in spectrum is associated with the coordination of NO to the $[CoTSPc]^{4-}$ species. A shift and increase in the monomeric peak of the [CoTSPc]⁴⁻ species on coordination of histidine and nitrite have been reported [47,48]. An increase and shifting of the monomer peak of [CoTSPc]⁴⁻ was also observed upon formation of an adduct between this species and oxygen. Oxygen was carefully excluded from the solutions containing NO and [CoTSPc]⁴⁻ and no spectral changes were observed for [CoTSPc]⁴⁻ in the absence of NO. Thus the spectral changes shown in Fig. 2 are associated with the formation of an adduct between NO and $[CoTSPc]^{4-}.$

X-ray photoelectron spectroscopy studies have indicated oxidation of the central metal in FePc and CoPc when the complexes are exposed to NO [41]. Electron transfer from Ni(II) to NO has also been implicated during coordination of NO to $[Ni(II)TSPc]^{4-}$, resulting in the formation of the $[(NO^{-})Ni(III)TSPc]^{4-}$ species [39]. Oxidation of Co(II)Pc to a Co(III)Pc species was also implicated on interaction of NO with CoPc [42]. We suggest that oxidation of the central metal also occurs on coordination of NO to the [CoTSPc]⁴⁻ species, forming a Co(III)TSPc-NO complex. Oxidation of [CoTSPc]⁴⁻ using chemical oxidants (e.g. bromine) resulted in the spectrum similar to that shown in Fig. 2b. The lack of an isosbestic point with the spectra of the starting complex in Fig. 2 is most likely a result of the two processes, coordination of NO to [CoTSPc]⁴⁻ and the subsequent electron transfer between the two molecules, occurring simultaneously.

In nitrosyl complexes, $\nu(NO)$ ranges from 1500 to 1900 cm⁻¹. $\nu(NO)$ for cobalt tetrakis(*N*-methyl-2-pyridyl)-

porphine [Co(2-TMpyP)(NO)] was observed at 1722 cm^{-1} [9] and for CoPc(NO) at 1680 cm⁻¹ [42]. IR spectra of the solid formed by reacting [Co(II)TSPc]⁴⁻ with NO showed a new band at 1730 cm^{-1} , in the range for coordinated NO. This value is higher than those reported for NO coordinated to cobalt porphyrins. Generally oxidized cobalt porphyrin complexes show $\nu(NO)$ values at higher frequencies than neutral complexes [12]. Thus the higher $\nu(NO)$ values for the (NO)CoTSPc complex could be a consequence of the oxidation of $[Co(II)TSPc]^{4-}$ to $[Co(III)TSPc]^{3-}$ following coordination of NO. As mentioned above, oxidation of $[Ni(II)TSPc]^{4-}$ to $[Ni(III)TSPc]^{3-}$ following coordination of NO has been observed. The IR spectra of the Ni(III)TSPc(NO⁻) complex showed ν (NO) at 1660 cm⁻¹ [39], much lower than the value reported here for the Co(III)TsPc(NO) complex. Vibrational frequencies of NO greater than 1700 cm⁻¹ have been associated with linear geometry of M-N=O and those of lower frequency to a bent geometry [39]. The observation of $\nu(NO)$ at 1730 cm⁻¹ suggests a bent geometry for the Co-NO bond in the Co-TSPc(NO) complex. Oxidation of NO to NO_2^- is likely following its coordination to CoTSPc. NO₂⁻ stretching frequencies were observed at 1401, 1306 and 830 cm^{-1} in Co(III)2-TMpyP(NO). We did not observe new IR bands in this region for the CoTSpc(NO) complex.

The coordination of NO to $[Co(II)TSPc]^{4-}$ can be represented by Eq. (1):

$$[\operatorname{Co}(\operatorname{II})\operatorname{TSPc}]^{4-} + \operatorname{NO} \underset{k_{r}}{\overset{k_{f}}{\rightleftharpoons}} [(\operatorname{NO}^{-})\operatorname{Co}(\operatorname{III})\operatorname{TSPc}]^{4-}$$
(1)

The number of NO molecules coordinated to the $[Co(II)TSPc]^{4-}$ species was determined using the standard equation [37,42]:

$$\log\left[\frac{A_{\rm eq} - A_0}{A_{\infty} - A_{\rm eq}}\right] = \log K + n\log[\rm NO]$$
⁽²⁾

where A_{eq} is the equilibrium absorbance at 667 nm, A_0 is the absorbance before addition of NO; A_{∞} , the absorbance after complete formation of the $[(NO^-)Co(III)TSPc]^{4-}$ complex, was determined from the final absorbance at 667 nm. Fig. 3a shows a plot of $\log[(A_{eq}-A_0)/(A_{\infty}-A_{eq})]$ versus $\log[NO]$. A linear plot with a slope $n=0.97\pm0.07$ was obtained, showing that only one molecule of NO is coordinated. The equilibrium constant (*K*) was determined from the intercept to be $3.0\pm0.5\times10^5$ dm³ mol⁻¹.

Plots of the observed rate constant (k_{obs}) versus the concentration of NO were linear (Fig. 3b), showing that the coordination is first-order in NO and obeys the rate law:

$$k_{\rm obs} = k_{\rm f} [\rm NO] + k_{\rm r} \tag{3}$$

where $k_{\rm f}$ is the rate constant for the formation of the $[(\rm NO^{-})\rm Co(III)\rm TSPc]^{4-}$ species according to Eq. (1) and $k_{\rm r}$ is the dissociation of this complex. Least-square analysis of the data presented in Fig. 3b gave $k_{\rm f} = 142 \pm 7 \, \rm dm^3 \, mol^{-1} \, s^{-1}$ from the slope, and $k_{\rm r} = 5.4 \pm 0.8 \times 10^{-4} \, s^{-1}$ was



Fig. 3. (a) Plot of $\log[(A_{eq}-A_0)/(A_{\infty}-A_{eq})]$ vs. $\log[NO]$. (b) Plot of the observed rate constant (k_{obs}) vs. the concentration of NO, for the formation of [(NO)⁻Co(III)TSPc]⁴⁻ species.

obtained from the intercept. Using these values of rate constants, the value of the equilibrium constant for NO coordination to $[Co(II)TSPc]^{4-}$ was estimated to be $K_1 = 2.6 \times 10^5 \text{ dm}^3 \text{ mol}^{-1}$ from the relationship $K_1 = k_f/k_r$, which is in excellent agreement, within experimental error, with the value determined above from the equilibrium data.

Table 1 compares the values of the rate constant for the coordination of NO to $[Co(II)TSPc]^{4-}$ with the values for its coordination to iron(II) porphyrin, metmyoglobin and hemoglobin. The values for the coordination of NO to the latter three molecules is much higher than the value for the coordination to $[Co(II)TSPc]^{4-}$. A low rate constant was also reported for the coordination of NO to manganese porphyrin complexes [11]. Axial ligand exchange reactions occur more slowly for CoPc than for FePc complexes [49]. The equilibrium constant for the coordination of NO to [$Co(II)TSPc]^{4-}$ was, however, much larger than for coordination of NO to the Fe(II) porphyrin, metmyoglobin and hemoglobin complexes (Table 1).

3.2. Electrocatalysis

Typical cyclic voltammograms for the reduction of NO on an unmodified GCE and on a GCE modified with $[Co(II)TSPc]^{4-}$ are shown in Fig. 4. On CoTSPc-GCE, a catalytic peak was observed at -0.96 V versus Ag|AgCl for the reduction of NO (Fig. 4b). The voltammogram for the reduction of NO on unmodified GCE is shown in Fig. 4a. The cyclic voltammogram of the adsorbed CoTSPc in buffer

alone did not show any peaks. The reduction currents for NO observed on GCE modified with $[Co(II)TSPc]^{4-}$ are much higher than the currents observed for the reduction of the same concentration of NO on an unmodified GCE. The peak currents for the reduction of NO on GCE modified with

Table 1 Equilibrium and rate constants for coordination of NO

Complex	$K (\mathrm{dm^3mol^{-1}})$	$k_{\rm f} ({\rm dm^3mol^{-1}s^{-1}})$	Ref.
Fe(III) porphyrin Metmyoglobin Hemoglobin [Co(II)TSPc] ⁴⁻	1.1×10^{3} 1.4×10^{4} 3.0×10^{5}	7.2×10^{5} 1.9×10^{5} 2.5×10^{7} 142	[14] [14] [14] this work



Fig. 4. Cyclic voltammogram for the reduction of 1.0×10^{-5} mol dm⁻³ NO on (a) unmodified GCE and (b) CoTSPc-GCE. Scan rate 100 mV s⁻¹.



Fig. 5. Plot of the variation of the catalytic currents for (a) reduction and (b) oxidation of NO on CoTSPc-GCE vs. the concentration of NO. Scan rate 100 mV s^{-1} .

 $[Co(II)TSPc]^{4-}$ increased with increase in NO concentration as shown in Fig. 5a. The modified electrode showed stability towards the reduction of NO in that the currents did not decrease appreciably with scan number. The peak at -0.96 V versus Ag|AgCl is almost at the same potential as that observed for reduction of NO (-0.93 V) on CoPcmodified GCE [42]. The pH of the media plays an important part in the catalytic reduction or oxidation of NO. The peak for the catalytic reduction of NO in water containing sodium sulfate was observed at -1.2 V versus Ag|AgCl. When the pH 7 buffer was employed the peak was observed at -1.1 V versus Ag|AgCl.

The cyclic voltammograms for the oxidation of NO on an unmodified GCE and on GCE modified with CoTSPc are shown in Fig. 6. There is a considerable enhancement in the oxidation currents of NO when GCE is modified with $[Co(II)TSPc]^{4-}$ compared with unmodified GCE. A weak broad peak is observed for NO on unmodified GCE near 1.1 V. On CoTSPc-GCE, the oxidation peak for NO is well resolved and observed at 1.08 V. The enhancement in oxidation currents when CoTSPc-GCE is employed shows that the $[Co(II)TSPc]^{4-}$ species acts as a catalyst for the oxidation of NO. The currents for the oxidation of NO on CoTSPc-GCE increased with increase in NO concentration, as shown in Fig. 5b. The lowest concentration of NO that could be determined using either the oxidation or reduction of NO on CoTSPc-GCE was of the order of 10^{-9} mol dm⁻³.

Bulk electrolysis of solutions containing NO at potentials for the catalytic reduction on CoTSPc-GCE gave $n \approx 5$, where n is the number of electrons involved in the reaction. This suggests that ammonia could be one of the reduction products of NO. Analysis of the solution obtained following bulk electrolysis did confirm the presence of ammonia with yields of about 25%. The current efficiency for ammonia production was determined to be 89%. Hydroxylamine was also found to be one of the products.



Fig. 6. Cyclic voltammogram for the oxidation of 2.1×10^{-4} mol dm⁻³ NO on (a) unmodified GCE and (b) CoTSPc-GCE. Scan rate 100 mV s⁻¹.

In conclusion, NO has been shown to coordinate to $[Co(II)TSPc]^{4-}$. The coordination is accompanied by electron transfer from the central Co(II) metal and the formation of $[(NO^-)Co(III)TSPc]^{4-}$ species. The rate constant for the formation of this species is much lower than those reported for the interaction of NO with metmyoglobin, iron(II) porphyrin and hemoglobin. $[Co(II)TSPc]^{4-}$ adsorbed on GCE catalyses both the reduction and oxidation of NO. The lowest concentration of NO that could be detected on GCE modified with $[Co(II)TSPc]^{4-}$ was of the order of 10^{-9} mol dm⁻³.

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