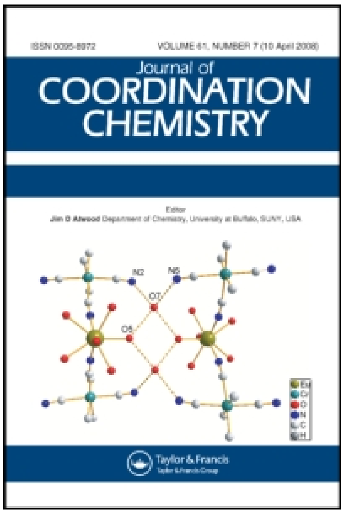

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INTERACTIONS OF COBALT(II) TETRASULFOPHTHALOCYANINE WITH NITRITE IN THE PRESENCE OF NITRATE AND PERCHLORATE IONS

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Spectroscopic changes observed on addition of nitrite to solutions of cobalt(II) tetrasulfophthalocyanine ($[Co(II)TSPc]^{4-}$) in the presence of NO_3^- or ClO_4^- are reported. There is spectroscopic evidence for the oxidation of $[Co(II)TSPc]^{4-}$ to a $[Co(III)TSPc]^{3-}$ species in the presence of nitrite ions. Equilibrium and kinetic studies for the interaction between $[Co(II)TSPc]^{4-}$ and NO_2^- are reported. The rate was found to be first order in both $[Co(II)TSPc]^{4-}$ and NO_2^-. The rate constant for the forward reaction, $k_f = 1.6 \times 10^{-4}$ $dm^3 mol^{-1} s^{-1}$ was determined at 20°C for the interaction between nitrite ions and $[Co(II)TSPc]^{4-}$ in the presence of NO_3^- or ClO_4^- ions.

Keywords: Nitrite; nitrate; perchlorate; cobalt; phthalocyanine; kinetics

INTRODUCTION

The reduction of nitrogen oxyanions is of interest for several reasons including the synthesis of useful chemicals such as ammonia and hydroxylamine, and the treatment of waste containing these ions. Nitrates are used extensively in detergents and fertilizers, and hence there is concern about the possible contamination of water by nitrate ions. In addition, waste originating from nuclear plants contains high levels of nitrate and nitrite, causing environmental concerns. The electrochemical and chemical reduction

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* Corresponding author.

and analyses of nitrate and nitrite ions continues to receive considerable attention.[1-12] The mechanism of the reduction of these species is very complex. The nature of the products of reduction depend on pH, coexisting ions and the choice of electrode material, among other things.

Metallophthalocyanine (MPc, Pc = phthalocyanine dianion) complexes, have been used in modifying conventional electrodes such as carbon, nickel or iron, resulting in a considerable increase in the activity of the electrode. For example, the potential for the oxidation of sulphur-containing compounds such as cysteine is greatly lowered when electrodes are coated with MPc complexes.[13-17] Corrosion of metallic electrodes is greatly reduced when the electrodes are coated with MPc species.[6] It is however, important to note that coating metallic iron with FePc did not increase the catalytic activity of this electrode towards the reduction of nitrate ions.[6]

Electrodes incorporating cobalt(II) phthalocyanine derivatives are sensitive to nitrite ion.[18] It was suggested that the high electron density around the central Co(II) ion favours the interaction between nitrite ion and the cobalt phthalocyanine species. Spectroscopic changes observed when solutions of NO_2^- were added to cobalt(II) 2,9,16,23-*tetra*(*tert*-butylphthalocyanine) (Co(II)TTBPc) solution, were attributed to the coordination of NO_2^- to CoTTBPc.[18] The selectivity of CoTTBPc for NO_2^- was attributed to this coordination. A study of the catalytic activity of the first row transition metal phthalocyanines for the reduction of nitrate and nitrite ions revealed a low catalytic activity for CoPc when compared to CuPc, FePc and NiPc.[19] In this work, we present equilibrium and kinetic studies for the interaction of NO_2^- with the cobalt(II) tetrasulfophthalocyanine ($[Co(II)TSPc]^{4-}$) complex.

EXPERIMENTAL

Cobalt(II) tetrasulfophthalocyanine, $Na_4[Co(II)TSPc]$, was prepared and purified according to the method of Weber and Busch.[20] Kinetic and equilibrium studies were run at 20 ± 1°C and monitored with the Cary 1E UV/Visible spectrophotometer. We monitored the disappearance of the spectrum due to $[Co(II)TSPc]^{4-}$ and the appearance of the spectrum due to the product formed following the addition of sodium nitrite to solutions of $[Co(II)TSPc]^{4-}$ in water. The ionic strength of the solution containing nitrite and the $[Co(II)TSPc]^{4-}$ was adjusted to $1.0\,mol\,dm^{-3}$ with sodium nitrate or sodium perchlorate. Triply distilled water was used for all experiments.

$[M(II)TSPc]^{4-}$ species form aggregates in aqueous solutions and hence the molar concentration may be difficult to determine. We used the published[21] extinction coefficient to estimate the concentration of the dimeric $\{[Co(II)TSPc]^{4-}\}_2$ species, with an absorption maxima at 624 nm. The concentration of this species was found to be near 1×10^{-5} mol dm^{-3}. The starting concentration of the $[Co(II)TSPc]^{4-}$ was kept constant for all kinetic and equilibrium data. The concentration of the nitrite ion ranged from 0.001 to 0.2 mol dm^{-3}, and was thus much larger than the concentration of the $[Co(II)TSPc]^{4-}$, hence ensuring *pseudo*-first order conditions for kinetic studies.

RESULTS AND DISCUSSION

Spectroscopic Characterization

Figure 1 shows the spectroscopic changes observed when NO_2^- (0.2 mol dm^{-3}) was added to an aqueous solution of $[Co(II)TSPc]^{4-}$ in the presence of ClO_4^-. It is now well established that metal(II) tetrasulfophthalocyanine ($[M(II)TSPc]^{4-}$) complexes form aggregates in solution.[21,22] The electronic absorption spectra of these species have been explained in terms of the monomer/dimer equilibrium. The lower energy absorption near 670 nm has been attributed to the monomeric species and the higher energy peak near 620 nm to the dimeric species.[21] The absorption spectrum shown in Figure 1(a), prior to the addition of NO_2^-, is typical of the $[M(II)TSPc]^{4-}$ species. The peak at 624 nm in Figure 1(a) is thus attributed to the dimeric $[Co(II)TSPc]^{4-}$ species and the peak at 665 nm to the monomeric species. On addition of NO_2^-, the absorption peak due to the dimeric species decreases in intensity, whereas there is an increase in the intensity of the absorption peak due to the monomeric species. The absorption maximum gradually shifts from 665 to 670 nm with time. The changes occur with a diffuse isosbestic point near 640 nm. The fact that the isosbestic point is not sharp suggests that constant stoichiometry is not maintained. The increase in absorption due to the monomeric species followed by a shift to lower energy was observed previously[21] when oxygen was bubbled through an alkaline solution of $[Co(II)TSPc]^{4-}$. The final spectrum in this reaction was attributed to the formation of an adduct between oxygen and $[Co(II)TSPc]^{4-}$. These spectroscopic changes were not observed in neutral media without heating the solution.[21] We tested the effects of residual oxygen by monitoring the spectra at 20°C of unpurged solutions of

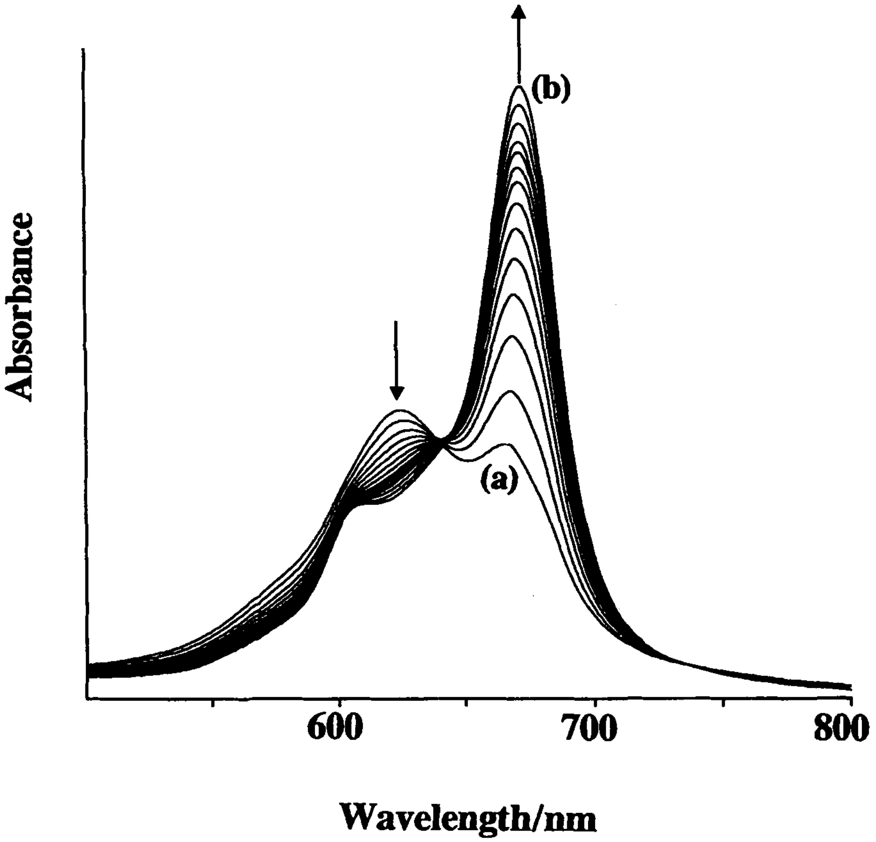

FIGURE 1 Absorption spectroscopic changes observed on addition of NO_2^- (0.2 mol dm^{-3}) to solutions of $[Co(II)TSPc]^{-4}$ in water. Ionic strength, $\mu = 1.0$ mol dm^{-3} in ClO_4^-, T = 20°C; (a) spectrum before addition of NO_2^- and (b) final spectrum observed after 4 h following the addition of NO_2^-.

$[Co(II)TSPc]^{4-}$ in the absence of nitrite. No significant changes were observed during 24 h. Thus, the changes shown in Figure 1 are due to the interaction between nitrite and $[Co(II)TSPc]^{4-}$. The final spectrum with a peak at 670 nm, Figure 1(b), is similar to that obtained on oxidation of $[Co(II)TSPc]^{4-}$ to $[Co(III)TSPc]^{3-}$,[23] and to the spectrum observed on addition of chemical oxidants such as bromine or ferric chloride to solutions of $[Co(II)TSPc]^{4-}$. Thus, the final spectra obtained on addition of nitrite to $[Co(II)TSPc]^{4-}$ are attributed to the oxidation of the central metal ion with the formation of $[Co(III)TSPc]^{3-}$. These changes are indeed typical of metal oxidation in MPc complexes.[24] Ring oxidation would result in considerable reduction in the intensity of the visible region spectrum.[24] When a reducing agent, *e.g.*, $NaBH_4$, was added to solutions containing NO_2^- and $[Co(II)TSPc]^{4-}$ at the end of the reaction between these species, the original spectrum due to the $[Co(II)TSPc]^{4-}$ was regenerated. This further confirms that the changes shown in Figure 1 are due to the formation of an oxidized species, which may be chemically reduced back to the starting species.

It is known[25] that nitrite disproportionates to form nitrate and nitric oxide, according to (1).

$$3NO_2^- + H_2O \rightleftharpoons 2NO_{(aq)} + NO_3^- + 2OH^- \quad (1)$$

The concentration of NO is low enough to be ignored in basic media, at $pH = 10$ or greater. About 5% of NO_2^- disproportionates to NO in near neutral conditions. Addition of nitrate to solutions of nitrite will push the equilibrium in (1) towards the nitrite side, making NO_2^- more dominant than NO. Both NO and NO_2^- are known to bind strongly to Co porphyrin complexes.[5]

Spectroscopic changes observed when NO_2^- was added to solutions of $[Co(II)TSPc]^{4-}$ in the presence of NO_3^- are shown in Figure 2. The original spectrum before the addition of nitrite and in the presence of NO_3^- shown in Figure 2(a), is different from the spectrum shown in Figure 1(a) in that in the former the dimeric absorption peak is more prominent than the peak due to the monomeric species. The peak due to the monomeric species occurs as a shoulder to the dimeric peak in Figure 2(a), whereas in Figure 1(a), the monomeric species shows a more defined peak. The monomer–dimer equilibrium is known to be dependent both on the ionic strength and on the ionic character of the medium;[26] thus the differences in the spectra shown in Figures 1(a) and 2(a) may be explained in terms of the differences in the ionic character of the medium. The spectroscopic changes observed in the presence of NO_3^- (Figure 2) were much slower than those observed in the presence of ClO_4^- (Figure 1). The only changes observed in the presence of NO_3^- involve a decrease in the dimer peak and an increase in the peak due to the monomeric species. The shift of the monomeric peak from 665 to 670 nm that was observed in the presence of ClO_4^- is not seen in Figure 2. When NO_3^- was added to solutions of $[Co(II)TSPc]^{4-}$ in the absence of NO_2^- and the spectra monitored with time, changes were insignificant. Also, when ClO_4^- was added to solutions of $[Co(II)TSPc]^{4-}$ in the absence of NO_2^- there was no noticeable change in the spectrum. Thus, there was no evidence for the coordination or reaction between $[Co(II)TSPc]^{4-}$ and ClO_4^- or NO_3^- in the absence of NO_2^-.

The autooxidation of the $[Co(II)TSPc]^{4-}$ species in the presence of NO_2^- is dependent on the medium. Earlier studies[26] on the interaction between

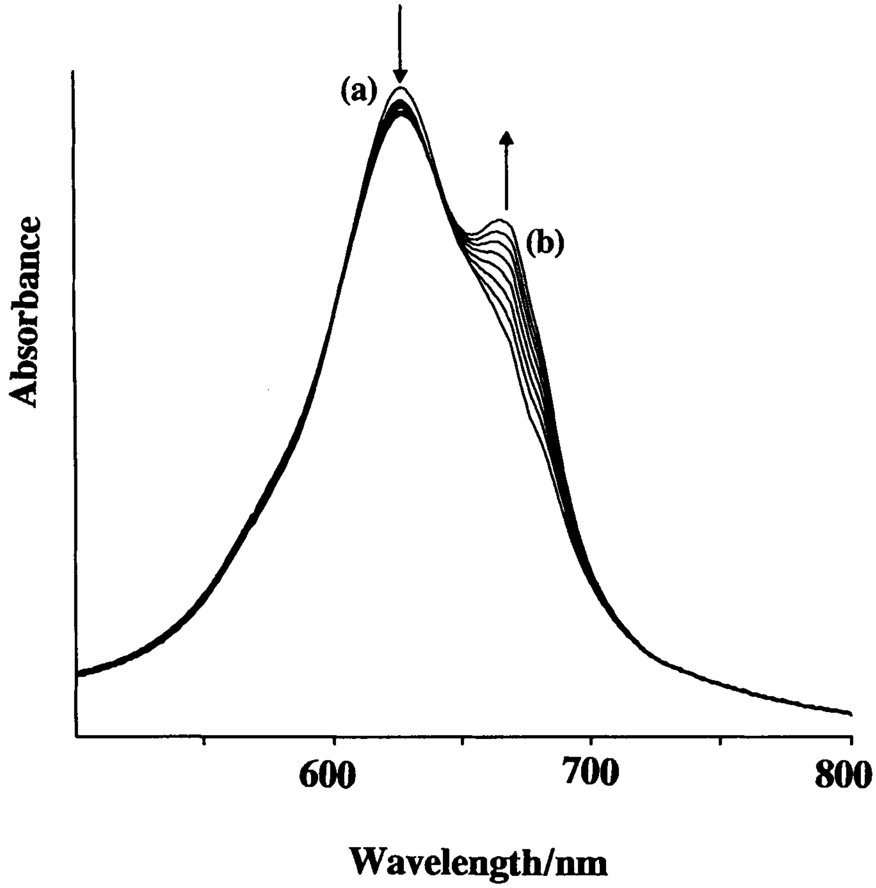

FIGURE 2 Absorption spectroscopic changes observed on addition of NO_2^- (0.1 mol dm^{-3}) to solutions of $[Co(II)TSPc]^{-4}$ in water. Ionic strength, $\mu = 1.0\,mol\,dm^{-3}$ in NO_3^-, $T = 20°C$; (a) spectrum before addition of NO_2^- and (b) final spectrum observed after 2 h following the addition of NO_2^-.

these species in water gave no evidence of the oxidation of $[Co(II)TSPc]^{4-}$ to $[Co(III)TSPc]^{3-}$. However, autooxidation of the $[Co(II)TSPc]^{4-}$ species was observed[26] in the presence of imidazole and cyanide ligands. We, however, observed significant spectroscopic changes when NO_2^- was reacted with $[Co(II)TSPc]^{4-}$ in water without added ions.

In aqueous solution, the $[Co(II)TSPc]^{4-}$ species is expected to contain water molecules in axial positions[22] and may thus be represented as $[(H_2O)_2Co(II)TSPc]^{4-}$. One or both of the water molecules may be replaced by more strongly binding ligands. Axial ligand exchange substitutions in porphyrin and phthalocyanine complexes are dissociative, resulting in the formation of a highly reactive 5-coordinate intermediate.[27–29] Equations (2) and (3) thus represent the replacement of the first water molecule by nitrite ions.

$$[(H_2O)_2Co(II)TSPc]^{4-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [(H_2O)Co(II)TSPc]^{4-} + H_2O \qquad (2)$$

$$[(H_2O)Co(II)TSPc]^{4-} + NO_2^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [(H_2O)(NO_2^-)Co(II)TSPc]^{5-} \qquad (3)$$

$$[(H_2O)Co(II)TSPc]^{4-} + NO \rightleftharpoons [(H_2O)(NO)Co(II)TSPc]^{4-} \qquad (4)$$

Equation (2) represents the formation of the 5-coordinate intermediate prior to the coordination of the nitrite ion. In the presence of excess nitrate there will be negligible amounts of nitric oxide, and equation (3) will dominate. Near neutral pH values that are applicable in this work and in the absence of nitrate ions, about 5% of nitrite is expected to disproportionate into nitric oxide and nitrate.[5] It is likely that the nitric oxide thus formed will also coordinate to $[(H_2O)Co(II)TSPc]^{4-}$ according to equation (4). Nitric oxide is an electron deficient ligand and it is known to have a strong affinity towards Co(II). However, because of the relatively small amount of NO present under neutral pH conditions, the coordination of NO to $[(H_2O)Co(II)TSPc]^{4-}$ is not expected to play a significant role when compared to the coordination of NO_2^-.

Kinetic and Equilibrium Studies in the Presence of NO_3^-

Equilibrium data for the interaction between NO_2^- and $[(H_2O)_2Co(II)TSPc]^{4-}$ in the presence of NO_3^- were analysed by standard spectrophotometric techniques using equation (5),

$$\log[(A_{eq} - A_0)/(A_\infty - A_{eq})] = \log K + n\log[NO_2^-] \qquad (5)$$

where A_{eq} is the equilibrium absorbance at 665 nm corresponding to the formation of the monomeric $[(H_2O)(NO_2^-)Co(II)TSPc]^{5-}$ complex and A_0 is the absorbance at 665 nm corresponding to zero percent formation of this complex. A_∞ is the absorbance for the complete formation of the complex was estimated from the final spectrum obtained after three half-lives. Plots of $\log[(A_{eq} - A_0)/(A_\infty - A_{eq})]$ *vs* $\log[NO_2^-]$, Figure 3, gave straight lines with slopes that were close to unity ($n = 1.00 \pm 0.05$). The value of unity for n shows that one mol of NO_2^- is coordinated to the $[Co(II)TSPc]^{4-}$ species. An equilibrium constant $K = 4.7 \pm 0.8\,dm^3\,mol^{-1}$ was obtained from the

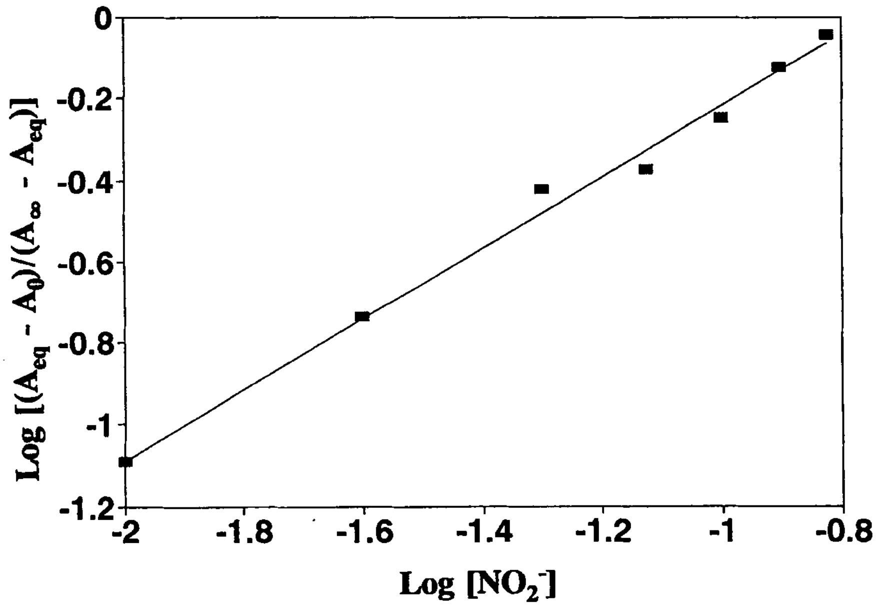

FIGURE 3 Plots of $\log[(A_{eq} - A_0)/(A_\infty - A_{eq})]$ *vs* $\log[NO_2^-]$ for the interaction between $[Co(II)\ TSPc]^{-4}$ and NO_2^-. Ionic strength $\mu = 1.0\,mol\,dm^{-3}$ in NO_3^-, $T = 20°C$.

intercept. The value of the equilibrium constant is much smaller than the values reported for axial ligand exchange reactions of CoPc complexes[30] (Table I). Equilibrium constants this low have been reported for the substitution of the second ligand in FePc complexes.[28,31,32] Coordination of CN^- and other ligands to $(L)_2MPc$ complexes normally occurs in a stepwise manner with the substitution of each ligand giving distinct spectroscopic changes in some cases.[28] We obtained no evidence of coordination of two nitrite ions to the $[Co(II)TSPc]^{4-}$ complex.

Pseudo-first order conditions were maintained since the concentration of NO_2^- was much larger than that of the $[(H_2O)_2Co(II)TSPc]^{4-}$ complex. The rate law for the dissociative mechanism given by equations (2) and (3) is given by equation (6).[28,32,33]

$$k_{obs} = k_1 k_2 [NO_2^-]/k_{-1}[H_2O] + k_{-2} \qquad (6)$$

Equation 6 is obeyed by axial ligand substitution reactions in phthalocyanines and porphyrins, with the reaction being first order in both the MPc complex and the entering ligand.[28,29,31] Linear plots for the formation of the monomeric complex, with absorption maxima at 665 nm in Figure 2,

TABLE I Equilibrium and kinetic data for axial ligand exchange reactions in cobalt(II) phthalocyanine complexes,[a] at 20°C

Complex	L^b	E^c	K^d ($dm^3 mol^{-1}$)	k_f^e ($dm^3 mol^{-1} s^{-1}$)	$k_r^e s^{-1}$	*Ref.*
$CoPc(DMSO)_2$	DMSO	py	1.6×10^2	7.7×10^{-3}	5.0×10^{-5}	30
$[(H_2O)_2CoTSPc]^{-4f}$	H_2O	NO_2^-	4.7	1.6×10^{-4}	2.9×10^{-6}	this work
$[(H_2O)_2CoTSPc]^{-4g}$	H_2O	NO_2^-		1.6×10^{-4}	4.6×10^{-6}	this work

[a]Solvents: py = pyridine, DMSO = dimethylsulfoxide. [b]L = leaving ligand. [c]E = entering ligand. [d]K = equilibrium constant. [e]Constants k_f and k_r as described in the text. [f]Ionic strength, $\mu = 1.0$ mol dm^{-3} in NO_3^-. [g]ionic strength, $\mu = 1.0$ mol dm^{-3} in ClO_4^-.

were obtained for $\log(A_\infty - A_t)$ (where A_t is the absorbance at 665 nm after time t) *versus* time. These plots confirm that the reaction has a first order dependence on the $[Co(II)TSPc]^{4-}$ species over three half-lives. The slopes of the plots of $\log(A_\infty - A_t)$ *versus* time gave the observed rate constant, k_{obs} and plots of k_{obs} *versus* the concentration of NO_2^- were also linear (Figure 4(a)), showing that the reaction is first order in NO_2^- and that equation (6) is obeyed for the reaction of $[Co(II)TSPc]^{4-}$ with NO_2^- in the presence of NO_3^-. The slope of the plot in Figure 4(a) gave the rate constant for the forward reaction, $k_f = k_1 k_2 / k_{-1}[H_2O] = 1.6 \pm 0.1 \times 10^{-4}$ dm^3 mol^{-1} s^{-1}. The intercept gave an estimate of the rate constant for the reverse reaction $k_r = k_{-2} = 2.9 \pm 1.0 \times 10^{-6}$ s^{-1}. These values k_f and k_r are much lower than the values reported for axial ligand exchange reactions in CoPc complexes[30] (Table I). The value of the equilibrium constant determined from k_f/k_r is 55 dm^3 mol^{-1}, much larger than the value of 4.7 dm^3 mol^{-1} obtained above. The discrepancy in the equilibrium constant could reflect the fact that the coordination of NO_2^- to the $[Co(II)TSPc]^{4-}$ species is complicated by a possible slow transformation to the oxidized $[Co(III)TSPc]^{3-}$ species.

Kinetic Studies in the Presence of ClO_4^-

In comparison with the reaction between NO_2^- and $[Co(II)TSPc]^{4-}$ in the presence of nitrate where the spectroscopic changes (Figure 2) were assigned only to the binding of the former to the latter, we associate the changes observed in Figure 1 for the interaction of NO_2^- with $[Co(II)TSPc]^{4-}$ in the presence of ClO_4^- with the axial coordination of the NO_2^- species followed by the autooxidation of the resulting complex and the formation of $[Co(III)TSPc]^{3-}$. The autooxidation of the $[Co(II)TSPc]^{4-}$ species to $[Co(III)TSPc]^{3-}$ implies that the reduction of the coordinated NO_2^- species occurs in the process. The presence of a diffuse isosbestic point in Figure 1 may be explained by the presence of the three species in

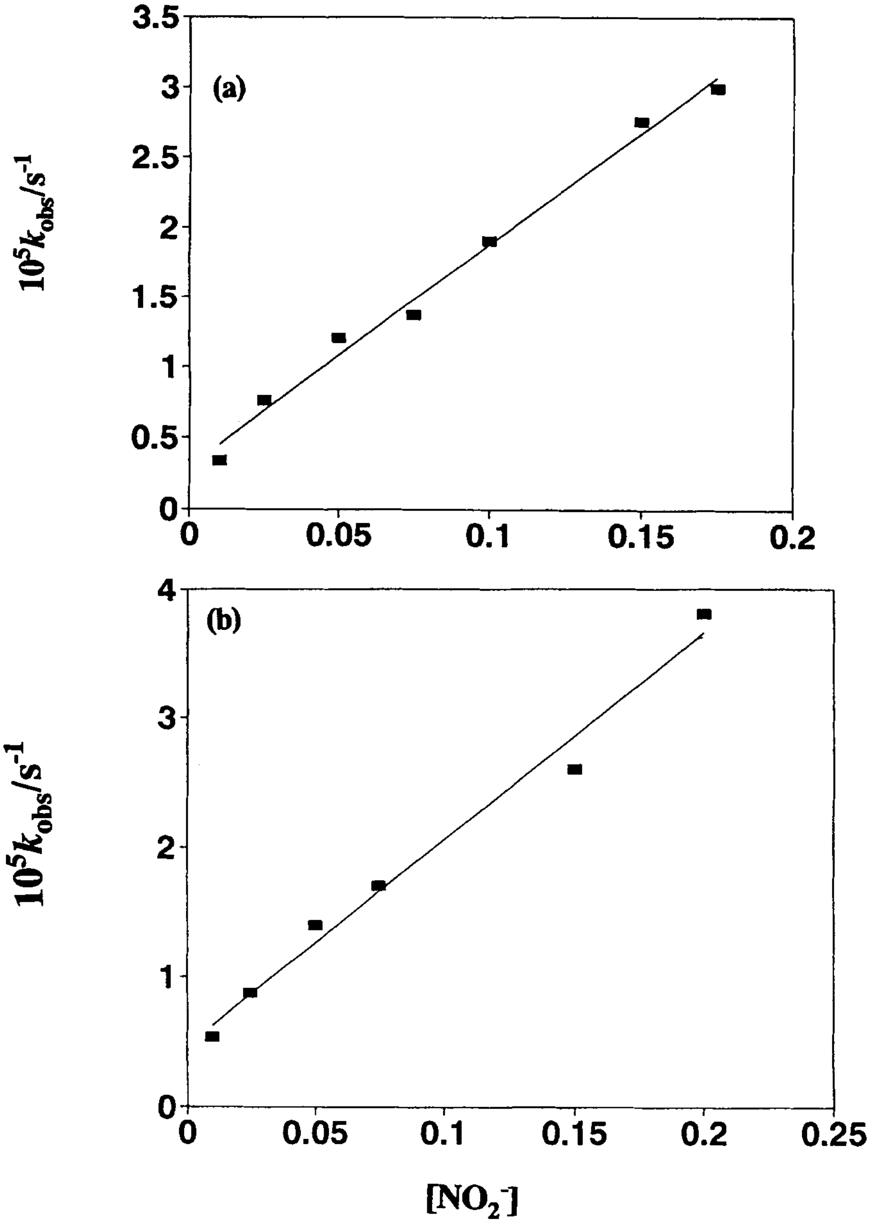

FIGURE 4 Plots of observed rate constants, k_{obs} *versus* [NO_2^-] (a) $\mu = 1.0$ mol dm^{-3} in NO_3^- and (b) $\mu = 1.0$ mol dm^{-3} in ClO_4^-, $T = 20$°C.

solution. The determination of accurate equilibrium data for the reaction in presence of ClO_4^- was complicated by the formation of the oxidized species following the coordination of nitrite to the $[Co(II)TSPc]^{4-}$ species.

Kinetic data for the interaction of NO_2^- with $[Co(II)TSPc]^{4-}$ was studied by monitoring the formation of the spectrum due to the oxidation product in Figure 1, with the peak maximum at 670 nm. The slopes of the linear plots of $\log(A_\infty - A_t)$ *versus* time gave k_{obs} and the plots of k_{obs} *versus* the concentration of NO_2^- were linear (Figure 4(b)), showing that equation (6) is obeyed and that the reaction is first order in both NO_2^- and the $[Co(II)TSPc]^{4-}$ species over three half-lives. From Figure 4(b), k_f was found to be $1.6 \pm 0.1 \times 10^{-4}$ dm^3 mol^{-1} s^{-1} and k_r was $4.6 \pm 0.8 \times 10^{-6}$ s^{-1}. These values are again much lower than the values reported for axial ligand substitution in CoPc complexes[30] (Table I). Using these values of k_r and k_f, an equilibrium constant of 34 dm^3 mol^{-1} was obtained.

The rate constants for the forward reaction, k_f, are a measure of the ease of dissociation of the leaving ligand and the ease of coordination of NO_2^- to the $[(H_2O)_2Co(II)TSPc]^{4-}$ species. For both the electrolytes, NO_3^- and ClO_4^-, k_f is much larger that k_r, the rate constant for the dissociation of nitrite from the products, hence showing that the products formed are relatively stable.

Kinetic and equilibrium studies for the reaction between nitrite and $[Co(II)TSPc]^{4-}$ give evidence for the interaction between these species. There is spectroscopic evidence for the oxidation of the central metal in $[Co(II)TSPc]^{4-}$ following addition of nitrite in the presence of perchlorate, and the formation of $[Co(III)TSPc]^{3-}$. Co(III)Pc species are known to have a much lower catalytic activity than Co(II)Pc species, hence the formation of the former in the presence of nitrite would inhibit the catalytic activity of cobalt phthalocyanine species. Spectroscopic changes reported in this work were not observed when NO_2^- was added to solutions of $[Cu(II)TSPc]^{4-}$, $[Fe(II)TSPc]^{4-}$ or $[Ni(II)TSPc]^{4-}$ species.

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