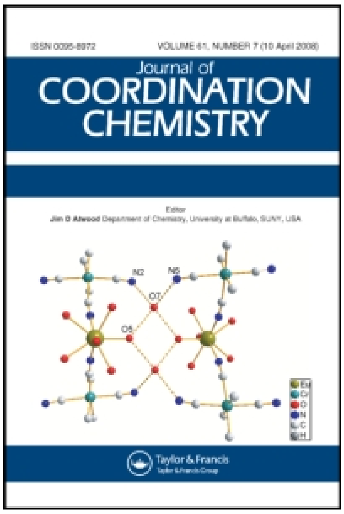

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

KINETICS AND MECHANISM OF THE INDUCED REDOX REACTION OF [Ni(CYCLAM)]2 PROMOTED BY SO_5-

Helena Redigolo Pezza[a]; Nina Coichev[b]
[a] Universidade Estadual Paulista, Instituto de Quimica, Araraquara, SP, Brazil [b] Universidade de ãTo Paulo, Instituto de Quimica, ãTo Paulo, SP, Brazil

To cite this Article Pezza, Helena Redigolo and Coichev, Nina(1999) 'KINETICS AND MECHANISM OF THE INDUCED REDOX REACTION OF [Ni(CYCLAM)]2 PROMOTED BY SO_5-', Journal of Coordination Chemistry, 47: 1, 107 — 119
To link to this Article: DOI: 10.1080/00958979908024546
URL: http://dx.doi.org/10.1080/00958979908024546

J. Coord. Chem., 1999, Vol. 47, pp. 107–119
Reprints available directly from the publisher
Photocopying permitted by license only

KINETICS AND MECHANISM OF THE INDUCED REDOX REACTION OF $[Ni(CYCLAM)]^{2+}$ PROMOTED BY $SO_5^{\bullet-}$

HELENA REDIGOLO PEZZA[a] and NINA COICHEV[b,*]

[a] *Universidade Estadual Paulista, Instituto de Química, Caixa Postal 355, CEP 14801-970, Araraquara, SP, Brazil;* [b] *Universidade de São Paulo, Instituto de Química, Caixa Postal 26.077, CEP 05599-970, São Paulo, SP, Brazil*

(Received 10 September 1997; Revised 25 November 1997; In final form 7 May 1998)

Oxidation of $[Ni(cyclam)]^{2+}$, cyclam = 1,4,8,11-tetraazacyclotetradecane, accelerated by sulfur dioxide, was studied spectrophotometrically by following the formation of $[Ni(cyclam)]^{3+}$ under the conditions: $[Ni(cyclam)]^{2+} = 6.0 \times 10^{-3}$ M; initial $[Ni(cyclam)]^{3+} = 8.0 \times 10^{-6}$ M; [cyclam] = 6.0×10^{-3} M; $[SO_2] = (1.0–5.0) \times 10^{-4}$ M and 1.0 M perchloric acid in oxygen saturated solutions at 25.0°C and ionic strength = 1.0 M. The oxidation reaction exhibits autocatalytic behavior in which the induction period depends on the initial Ni(III) concentration. A kinetic study of the reduction of Ni(III) by SO_2 under anaerobic conditions, and the oxidation of Ni(II), showed that the rate-determining step involves reduction of Ni(III) by SO_2 to produce the $SO_3^{\bullet-}$ radical, which rapidly reacts with dissolved oxygen to produce $SO_5^{\bullet-}$ and rapidly oxidizes Ni(II). The results clearly show a redox cycling process which depends on the balance of SO_2 and oxygen concentrations in solution.

Keywords: Nickel; cyclam; sulfur dioxide; peroximonosulfate

INTRODUCTION

The oxidation of some metal ions such as Co(II), Mn(II), Fe(II), Ni(II) and Cu(II) in the presence of dissolved oxygen and sulfur(IV) oxides, which undergoes simultaneous oxidation to S(VI), is of environmental interest, especially in the case of Fe(II)/(III) and Mn(II) because of their relative high abundance. Detailed kinetic studies showed that these ions can be important in the catalyzed autoxidation of SO_2.[1–4]

---

* Corresponding author. E-mail: ncoichev@quim.iq.usp.br

An extensive, recent review by Brandt and van Eldik reports on the importance of the transition metal catalyzed oxidation of sulfur(IV) oxides with emphasis on atmospheric-relevant processes and mechanisms.[5]

In the presence of suitable aqueous medium, formation of the metal ion in the +3 oxidation state can be followed. Some detailed kinetic and mechanistic studies have been done for the systems: Fe(III)/tris1,10-phenanthroline,[6] Cu(II)/Cu(III)/tetraglycine,[7] Co(II)/Co(III)/NH_3,[8] Fe(II)/Fe(III)/EDTA,[9] Fe(II), Mn(II), Co(II), Ni(II), Cu(II) and V(IV) with phthalocyanines,[10] Mn(III)/CDTA,[11] Co(II)/Co(III)/N_3^-,[12] Mn(II)/Mn(III)/N_3^-,[13] and Ni(II)/Ni(III) with peptides.[14]

A series of studies on Co(II) in aqueous azide solutions led to the development of an alternative analytical method for the determination of S(IV) in environmental samples and degraded hexafluoride.[15–19] The concentration of Co(III) complex formed exhibited a linear relationship with the initial sulfur(IV) oxide concentration.

In the present study we have investigated the kinetics and mechanism of $[Ni(cyclam)]^{2+}$, cyclam = 1,4,8,11-tetraazacyclotetradecane, oxidation in the presence of oxygen and SO_2, by following the spectral absorbance changes. This reaction is strongly accelerated by SO_2 and some very small amount of $[Ni(cyclam)]^{3+}$ (8.0×10^{-6} M) initially added.

The present study reports the combination of the reduction and induced oxidation studies, with evidence for a radical chain mechanism involving redox cycling. It is important to consider that in our experiments the metal ion was initially in the +2 oxidation state in the presence of SO_2 (reducing agent). For the first time it was possible to follow Ni(III) complex formation, in the presence of SO_2 and oxygen, under controlled experimental conditions. The autocatalytic behavior could be detected only after adding some Ni(III) from the beginning.

Linn *et al.*, studied the reduction of $[Ni(cyclam)]^{3+}$ under anaerobic and aerobic conditions, with *pseudo* first-order conditions in the presence of an excess of SO_2.[20,21] These reduction studies did not show the importance of the induced oxidation of $[Ni(cyclam)]^{2+}$ and the redox cycling, and could not be clearly explained by the data reported.

The $[Ni(cyclam)]^{3+}$ complex has an absorption peak at 206 nm ($\varepsilon = 2.8 \times 10^3\ M^{-1}\,cm^{-1}$) and 308 nm ($\varepsilon = 1.1 \times 10^4\ M^{-1}\,cm^{-1}$); $[Ni(cyclam)]^{2+}$ at 206 nm ($\varepsilon = 1.0 \times 10^4\ M^{-1}\,cm^{-1}$) and 308 nm ($\varepsilon = 17\ M^{-1}\,cm^{-1}$); and aqueous sulfur dioxide at 206 nm ($\varepsilon = 1.8 \times 10^3\ M^{-1}\,cm^{-1}$) and 308 nm ($\varepsilon = 57\ M^{-1}\,cm^{-1}$).[20] The cyclam ligand does not absorb at 308 nm.

EXPERIMENTAL

All reagents were of analytical grade (Merck or Aldrich Chemical) and deionized water was used to prepare all solutions. Nitrogen was used to deaerate solutions when it was required.

Stock solutions of sulfite (2.0×10^{-2} M) were prepared daily by dissolving $Na_2S_2O_5$ in deaerated water. To prepare diluted solutions of sulfite, a small volume of the stock solution was added to oxygen saturated water. $[Ni(cyclam)](ClO_4)_2$ was prepared as described in the literature.[22] Conversion of this complex to the corresponding Ni(III) compound was done by chemical oxidation using HNO_3.[23]

The UV/VIS spectra were recorded on a Cary 1E spectrophotometer, which was also used for kinetic measurements in the thermostated (25.0 ± 0.1 °C) cell compartment. In many experiments, air and oxygen saturated solutions were employed for which the oxygen concentration can be considered to be 2×10^{-4} M and 1.1×10^{-3} M, respectively, under the selected conditions at 1.0 M $HClO_4$.[5] All UV/VIS spectra were recorded using 1.0 M $HClO_4$ as a blank.

A fast oxygen detection system (OXYTECH), as described in earlier experiments,[24] was used to study the oxygen consumption during the SO_2 induced oxidation of Ni(II).

RESULTS AND DISCUSSION

In the present study, Ni(III) formation was followed when sulfite was added to an oxygen or air saturated acidic solution of $[Ni(cyclam)]^{2+}$.

Complementary studies were performed, under anaerobic conditions, following the reduction of $[Ni(cyclam)]^{3+}$ by SO_2 in the presence of a large excess of $[Ni(cyclam)]^{2+}$. The very high $[Ni(cyclam)]^{2+}$ concentration employed favors formation of $[Ni(cyclam)]^{3+}$ in aqueous solution, decreasing the conditional reduction potential.

As the literature reports high stability of the solutions of $[Ni(cyclam)]^{3+}$, in highly acidic solutions, we carried out our experiments in 1.0 M perchloric acid.[25,26] In neutral or basic solution, the stability drastically decreases with increasing pH, the Ni(III) promotes deprotonation of an amine group of cyclam followed by decomposition via ligand oxidation.[27]

SO_2 Induced Oxidation of $[Ni(cyclam)]^{2+}$

When the spectral changes of an acidic, air-saturated solution of $[Ni(cyclam)]^{2+}$ (6.0×10^{-3} M) are monitored for 6 days, no obvious spontaneous oxidation by oxygen to $[Ni(cyclam)]^{3+}$ was observed.

Oxidation of $[Ni(cyclam)]^{2+}$ in acidic, oxygen-saturated solutions was studied under conditions where $[Ni(cyclam)]^{2+}$ was always in large excess compared to Ni(III) and SO_2. After addition of sulfite solution, the formation of $[Ni(cyclam)]^{3+}$ was followed by the absorbance changes at 308 nm.

In the experiments, freshly prepared solutions were employed. An equal volume of oxygen saturated sulfite solution was mixed with an acidic oxygen saturated solution of a metal ion complex, with an excess of cyclam and some $[Ni(cyclam)]^{3+}$ initially added. In oxygen saturated solutions, the absorbance changes were much more significant as compared to air saturated solutions, as will be explained later. In all figures the composition of the final solution after the mixing is indicated.

The induced oxidation can be described by the overall reaction (eq. (**1**)):

$$2[Ni(cyclam)]^{2+} + SO_2 + O_2 \rightarrow 2[Ni(cyclam)]^{3+} + SO_4^{2-} \qquad (\mathbf{1})$$

Figure 1 reports the absorbance changes at 308 nm after successive additions of small volumes ($2.0 \times 10^{-5}\,dm^3$) of a sulfite stock solution (0.02 M) to $2 \times 10^{-3}\,dm^3$ of an acidic, oxygen-saturated solution of the metal complex. At this level of SO_2 concentration (2.5×10^{-4} M) in the

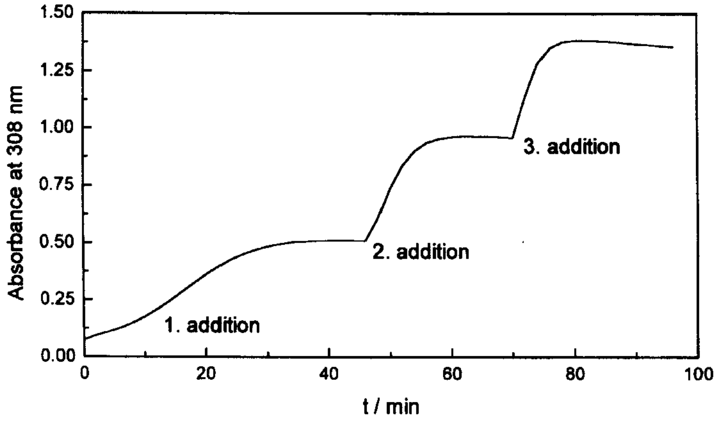

FIGURE 1 Effect of successive sulfite additions of $2.0 \times 10^{-5}\,dm^3$ of stock solution of sulfite (0.02 M) to $2.00 \times 10^{-3}\,dm^3$ of the oxygen-saturated working solution: $[Ni(cyclam)]_i^{3+} = 8.0 \times 10^{-6}$ M; $[Ni(cyclam)]^{2+} = 6.0 \times 10^{-3}$ M; $[SO_2]_i \cong 2 \times 10^{-4}$ M; $[cyclam] = 6.0 \times 10^{-3}$ M; $[HClO_4] = 1.0$ M; $T = 25$°C.

working solution, the total absorbance change (ΔA), after the limiting value has been reached, is constant for the same SO_2 concentration added (second addition), showing that enough oxygen is still available in the solution.

The induction period, which is evidence for autocatalytic behavior, depends on the initial concentration of $[Ni(cyclam)]^{3+}$ present. The induction period decreases after each successive sulfite addition (Figure 1). A similar induction period and autocatalytic behavior has been reported for the $Co(II)/Co(III)/N_3^-$,[12] $Mn(II)/Mn(III)/N_3^-$,[28] $Fe(II)/Fe(III)/H_2O$[1,3,29], $Co(II)/H_2O$[30] and $Mn(II)/Mn(III)/H_2O$[31] systems. These studies also showed that because of the nature of the autocatalytic process, the rate and the concentration of the metal ion in the +3 oxidation state depend on the employed SO_2 concentration. We believe that the same mechanism operates in the system under investigation.

The total absorbance change, ΔA, is a linear function of the initial SO_2 concentration ($[SO_2]_i$) up to 2.5×10^{-4} M (Figure 2). The stoichiometric relation, according to the general equation (eq. (1)) is $[Ni(III)] : [SO_2]_i = 2 : 1$. In our experiments, under the conditions shown in the linear portion of Figure 2, this stoichiometric relation, is $(0.19 \pm 0.03) : 1$, smaller due to chain propagation and termination reactions with radicals. This relation was calculated considering the absorbance change, due to $[Ni(cyclam)]^{3+}$ concentration, and $\varepsilon = 1.1 \times 10^4\,M^{-1}\,cm^{-1}$. For concentrations of SO_2 higher than 2.5×10^{-4} M, the linearity is not observed due to the partial reduction of the produced Ni(III) by SO_2, since, after some time, the

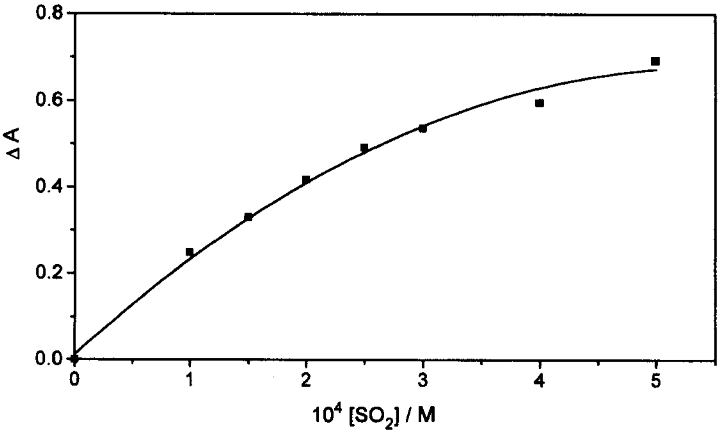

FIGURE 2 ΔA (total absorbance change) vs. $[SO_2]_i$ for the oxidation of $[Ni(cyclam)]^{2+}$. Conditions: $[Ni(cyclam)]^{2+} = 6.0 \times 10^{-3}$ M; $[Ni(cyclam)]_i^{3+} = 8.0 \times 10^{-6}$ M; $[cyclam] = 6.0 \times 10^{-3}$ M; $[HClO_4] = 1.0$ M; $T = 25°C$; optical path length = 0.88 cm.

concentration of dissolved oxygen in the solution is very low as compared to SO_2 still available in solution. This shows there is a balance between the oxygen and SO_2 concentrations, as will be discussed further.

The Olis Kinfit set of programs[32] was employed to fit the absorbance–time traces according to first order behavior (OLIS).

The *pseudo* first-order rate constants, k_{obs}, were calculated from the absorbance–time traces, neglecting the induction period during the first few minutes. The k_{obs} values were reproducible and depend linearly on the initial SO_2 concentration. The influence of the initial Ni(III) concentration can also be seen in Figure 3.

We believe that the mechanism operating in the present system is the same as for Co(II)/Co(III)/N_3^- (see Ref. [12]) and Fe(II)/Fe(III)/H_2O.[1,3,29] The same data treatment can be performed as described in Ref. [12]. The present results can also be described by a similar empirical rate law (eq. (**2**)), where $k_a = 42\,M^{-1}\,s^{-1}$ and $k_b = 7.4\,M^{-1}\,s^{-1}$. This equation is only valid when some small initial concentration of Ni(III) is added and $[SO_2]_i$ is smaller than 2.5×10^{-4} M.

$$k_{obs} = k_a[\mathrm{Ni(III)}]_i + k_b[SO_2]_i. \tag{2}$$

The values of k_{obs} are not affected by the concentration of Ni(II) in the range of (6–10) × 10^{-3} M; at higher concentrations, there is a problem with the solubility of $[\mathrm{Ni(cyclam)}](ClO_4)_2$.

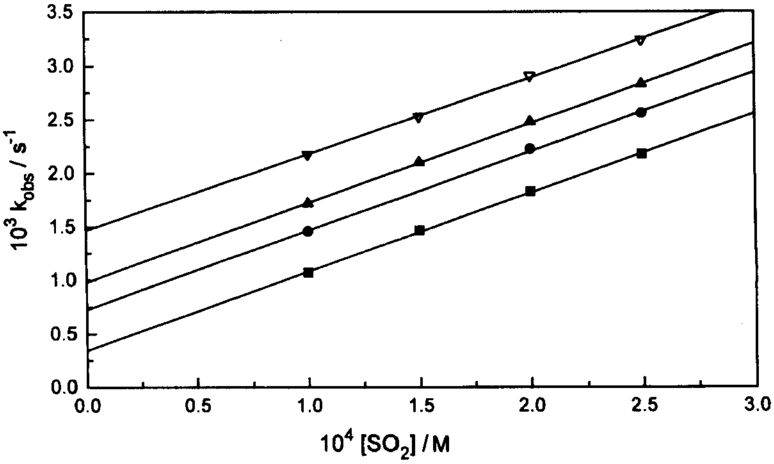

FIGURE 3 k_{obs} as a function of $[SO_2]_i$ for the oxidation of $[\mathrm{Ni(cyclam)}]^{2+}$ in the presence of added $[\mathrm{Ni(cyclam)}]^{3+}$. Conditions: $[\mathrm{Ni(cyclam)}]^{2+} = 6.0 \times 10^{-3}$ M; [cyclam] = 6.0×10^{-3} M; $[HClO_4] = 1.0$ M; $T = 25°C$; $[\mathrm{Ni(cyclam)}]_i^{3+}$: (▽) 3.4×10^{-5} M; (▲) 2.4×10^{-5} M; (●) 1.8×10^{-5} M; (■) 8.3×10^{-6} M.

With an excess of ligand as compared to [Ni(II)], a slightly higher absorbance change, ΔA was observed. Therefore an excess of cyclam, that is $[\mathrm{Ni(cyclam)}]^{2+} : [\mathrm{cyclam}] = 1:1$, was used in our experiments.

Influence of Oxygen Concentration. Evidence for Redox Cycling

Oxygen consumption during the oxidation of SO_2 and $[\mathrm{Ni(cyclam)}]^{2+}$ was followed by amperometric detection.[24] Figure 4 shows parallel experiments during which the oxygen consumption and the formation of $[\mathrm{Ni(cyclam)}]^{3+}$ were monitored. At an SO_2 concentration of 5×10^{-4} M in oxygen-saturated solution, formation of Ni(III) is more effective and, when the absorbance limit is reached, there is still some oxygen left in solution (Figure 4(a) and (b)). In air-saturated solution, formation of Ni(III) stops as soon as the oxygen has been used (Figure 4(c) and (d)). At that point, the excess SO_2 present in solution reduces Ni(III) to Ni(II). By introducing oxygen from air, Ni(III) is formed again initiating the redox cycling.

It is easy to observe a redox cycle when the SO_2 concentration is 1.5×10^{-3} M. There is a formation of a small amount of Ni(III) followed by reduction (Figure 4(e) and (f)), then introduction of more oxygen from air, by shaking the solution, since there is still SO_2 left in solution, the oxidation starts again (Figure 4(e)). Thus a crucial control over the SO_2 and O_2 concentration will determine in which oxidation state the nickel complex exists.

The redox cycling was also demonstrated for systems with Co(II), Mn(II) and Fe(II)/(III)[1,33] showing the important aspects under atmospheric conditions of the abatement of sulfur(IV) oxides.

Reduction of $[\mathrm{Ni(cyclam)}]^{3+}$ by SO_2

As the reduction of $[\mathrm{Ni(cyclam)}]^{3+}$ is the rate-determining step, it was studied under anaerobic and *pseudo* first-order conditions, *i.e.*, an excess of SO_2. The solution also contained a large excess of $[\mathrm{Ni(cyclam)}]^{2+}$ and was highly acidic in order to stabilize Ni(III) in aqueous solution. When sulfite is added to such a solution, the absorbance maximum at 308 nm decreases due to reduction of Ni(III) to Ni(II), according to the overall reaction (eq. (3)):

$$2[\mathrm{Ni(cyclam)}]^{3+} + SO_2 + 2H_2O \rightarrow 2[\mathrm{Ni(cyclam)}]^{2+} + SO_4^{2-} + 4H^+ \quad (3)$$

Pseudo first-order rate constants were obtained from the absorbance time traces at 308 nm, which exhibited excellent first-order behavior. The observed rate constants, k_{obs}, depend linearly on the SO_2 concentration, as

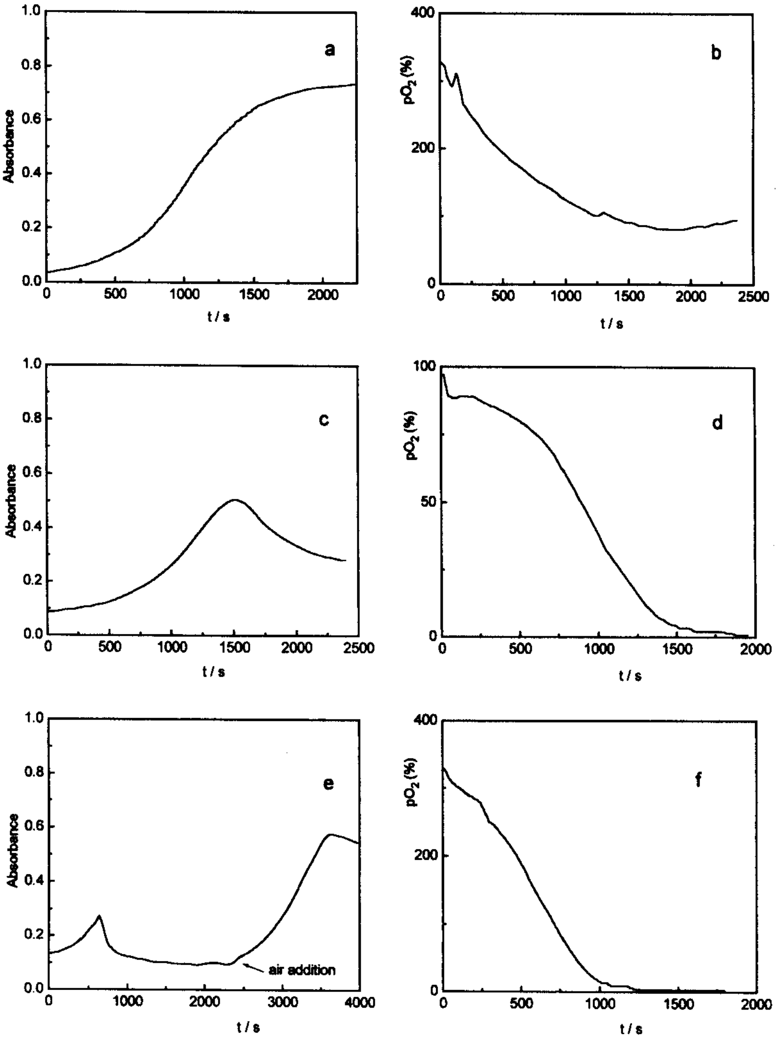

FIGURE 4 Absorbance changes at 308 nm and oxygen concentration as a function of time after the addition of sulfite to a $[Ni(cyclam)]^{2+}$ solution. Conditions: $[Ni(cyclam)]^{2+} = 6.0 \times 10^{-3}$ M; $[Ni(cyclam)]^{3+} = 8.0 \times 10^{-6}$ M; $[cyclam] = 6.0 \times 10^{-3}$ M; $[HClO_4] = 1.0$ M; $[SO_2]_i$: (a) and (b) 5.0×10^{-4} M oxygen-saturated solution; (c) and (d) 5.0×10^{-4} M air-saturated solution; (e) and (f) 15.0×10^{-4} M oxygen-saturated solution; $T = 25°C$; optical path length = 1.00 cm.

shown in Figure 5. The data can be discussed by the relationship in eq. (4):

$$k_{obs} = k_r[SO_2]_i, \qquad (4)$$

where $k_r = 10.8\ M^{-1}\ s^{-1}$ at 25.0°C.

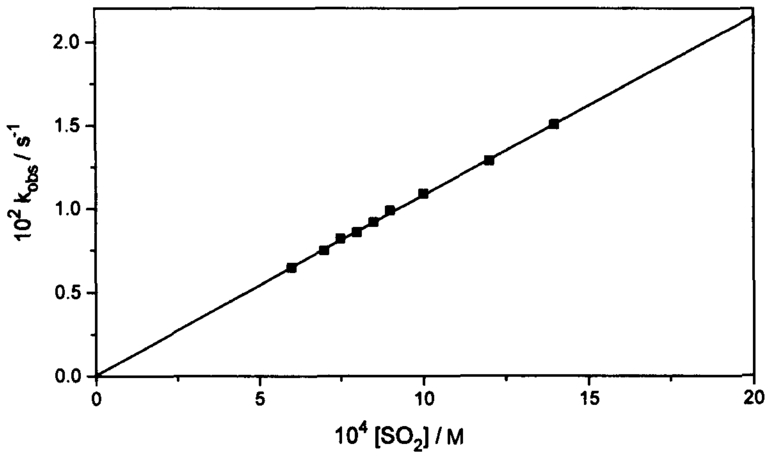

FIGURE 5 k_{obs} as a function of $[SO_2]_i$ for the reduction of $[Ni(cyclam)]^{3+}$. Conditions: $[Ni(cyclam)]_i^{3+} = 6.0 \times 10^{-5}$ M; $[Ni(cyclam)]^{2+} = 6.0 \times 10^{-3}$ M; $[HClO_4] = 1.0$ M; $T = 25°C$; absence of oxygen.

The kinetic data reported in the Figure 5 are qualitatively in close agreement with those reported for the oxidation of Ni(II) (Figures 3 and 6), demonstrating that the same rate-determining step must be operative during the reduction of Ni(III) by SO_2 and the oxidation of Ni(II) in the presence of oxygen and SO_2 in a cyclam solution.

Overall Mechanism

For a general autocatalytic reaction A → P the reaction sequence can be formulated as in (**5**):

$$\begin{aligned} &A + P \rightarrow B \\ &B \rightarrow (a + 1)P \quad \text{fast} \end{aligned} \qquad (5)$$

In this reaction sequence the formation of the intermediate B ($SO_3^{\bullet-}$ in the present study) is rate-determining and is followed by a series of successive fast steps. The rate law for such a process is given by the expression (**6**):[12,34]

$$dx/dt = k(A_0 - x)(P_0 + ax). \qquad (6)$$

Integration of this expression leads to:

$$\ln(P_0/A_0) - \ln(P_0 + ax) + \ln(A_0 - x) = -k(P_0 + aA_0)t, \qquad (7)$$

where $P_0 = [Ni(III)]_i$ and $A = [SO_2]_i$.

Ni(III) was introduced from the start to minimize the autocatalytic part of the process and the kinetic traces were only fitted from the point of maximum rate, *i.e.*, maximum $\Delta A/\Delta t$.

From eq. (**6**) it can be shown that the maximum rate is reached at $(P_0 + ax)/(A_0 - x) = a$. From this point on $(P_0 + ax)$ will increase to $(P_0 + aA_0)$, whereas $(A_0 - x)$ will decrease to zero. Since $\ln(P_0/A_0)$ will be constant during the reaction, it follows that the later part of the kinetic trace is dictated by $\ln(A_0 - x)$, which exhibits first-order behavior with the observed rate constant given in (**8**):

$$k_{obs} = k(P_0 + aA_0). \qquad (\mathbf{8})$$

With the combination of eqs. (**2**) and (**8**), considering the $[SO_2]$ range $(1.0–2.5) \times 10^{-4}$ M, the data can be fitted to eq. (**9**), as shown in Figure 6.

$$k_{obs} = k\{[Ni(III)]_i + 0.18[SO_2]_i\}. \qquad (\mathbf{9})$$

In fact, the relation $a = [Ni(III)] : [SO_2]_i = 0.18$, obtained from the spectrophotometric data, was 0.19 (Figure 2).

Mechanisms

Our studies on the induced oxidation of $[Ni(cyclam)]^{2+}$ clearly show evidence for a radical chain mechanism.

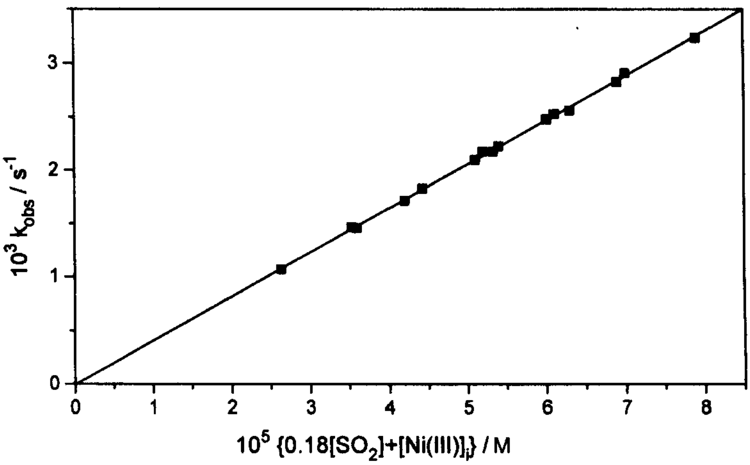

FIGURE 6 Linear dependence of k_{obs} with $\{0.18[SO_2]_i + [Ni(III)]_i\}$ for the oxidation of $[Ni(cyclam)]^{2+}$. Conditions: as indicated in Figure 3.

The catalytic effect of the initial Ni(III) and the oxygen dependence show that the rate-determining step is generation of the $SO_3^{\bullet -}$ radical due to the reduction of Ni(III) initially present at very low concentration (eq. (**10**)). It shows that the initial Ni(III), even at low concentrations, has a marked effect on the induction period.

The mechanism presented in Scheme 1, is similar to the one proposed in earlier studies for the Co(II)/Co(III)/N_3^-,[12] Mn(II)/Mn(III)/N_3^-,[13] and Fe(II)/Fe(III)/H_2O[1,29] systems, where it is discussed on the basis of available literature and includes several steps considering the different radicals formulated as: $SO_3^{\bullet -}$, $SO_5^{\bullet -}$, $SO_4^{\bullet -}$ and $OH^\bullet$.

The following scheme describes only the main reactions involving the reduction and the oxidation steps that account for the oxidation of $[Ni(cyclam)]^{2+}$ promoted by the strongly oxidizing $SO_5^{\bullet -}$ ion. There is need for the initiator, $[Ni(cyclam)]^{3+}$, to get the reaction started.

The chain propagation, the product formation and termination reactions are described in detail in Refs. [12] and [13].

Initiation of the oxidation of $[Ni(cyclam)]^{2+}$ induced by SO_2, in absence of added Ni(III) is probably due to low concentrations of Fe(III), present as unavoidable impurities in chemicals ($HClO_4$, $Ni(ClO_4)_2$, *etc.*) and solvents (ethyl alcohol, ethyl ether, acetone) utilized in the synthesis of the $[Ni(cyclam)](ClO_4)_2$ and $[Ni(cyclam)(NO_3)_2](ClO_4)$. Other trace metal impurities and peroxide (possibly in the ether) must also be considered.

Initiation in the presence of added $[Ni(cyclam)]^{3+}$:

$$[Ni(cyclam)]^{3+} + SO_2 + H_2O \rightarrow [Ni(cyclam)]^{2+} + SO_3^{\bullet -} + 2H^+ \quad \text{slow} \qquad \textbf{(10)}$$

or some trace Fe(III) impurities (see eq. (**15**))

Autocatalysis:

$$SO_3^{\bullet -} + O_2 \rightarrow SO_5^{\bullet -} \quad 1.1 \times 10^9\ M^{-1}\,s^{-1} \quad \text{(Ref. [5])} \qquad \textbf{(11)}$$

$$[Ni(cyclam)]^{2+} + SO_5^{\bullet -} + H^+ \rightarrow HSO_5^- + [Ni(cyclam)]^{3+} \qquad \textbf{(12)}$$

$$[Ni(cyclam)]^{2+} + HSO_5^- \rightarrow [Ni(cyclam)]^{3+} + SO_4^{2-} + OH^\bullet \qquad \textbf{(13)}$$

or

$$[Ni(cyclam)]^{2+} + HSO_5^- \rightarrow [Ni(cyclam)]^{3+} + SO_4^{\bullet -} + OH^- \qquad \textbf{(14)}$$

SCHEME 1 The mechanism of the oxidation of $[Ni(cyclam)]^{2+}$ in the presence of SO_2 and O_2.

It is difficult to exclude trace concentrations of Fe(III) even in highly purified water. Previous analyses showed that iron may be present at concentrations of 8×10^{-9} to 5×10^{-8} M.[2]

If Fe(III) is present it reacts with SO_2 and generates $SO_3^{\bullet -}$ radical,

$$\mathrm{Fe(III)} + SO_2 + H_2O \rightarrow \mathrm{Fe(II)} + SO_3^{\bullet -} + 2H^+ \qquad \textbf{(15)}$$

which rapidly forms peroxomonosulfate radical by reaction with oxygen (eq. (**11**)). The $SO_5^{\bullet -}$ then can oxidize $[\mathrm{Ni(cyclam)}]^{2+}$ to $[\mathrm{Ni(cyclam)}]^{3+}$ (eq. (**12**)).

In our experiments, with no Ni(III) added, the induced oxidation is very slow, for example when $SO_2 = 2 \times 10^{-4}$ M the formation of Ni(III) begins after 40 min (compare with Figure 1, where [Ni(III)] added is 8×10^{-6} M).

The studies described here provide an understanding of the redox cycling on the induced oxidation of $[\mathrm{Ni(cyclam)}]^{2+}$, with simultaneous oxidation of SO_2 to SO_4^{2-}. It shows the importance of several transition metal ions, present even at a relative small concentration, on the oxidation SO_2 by oxygen. In this case, the combination of kinetic studies with the equilibrium complex formation allowed us to follow the changes in the oxidation state of the metal ion *via* spectrophotometric measurements. The $[\mathrm{Ni(cyclam)}]^{2+}$ is a very stable complex, $\log K = 22.2$ (25°C, ionic strength 0.1 M),[35] and it has been shown that in perchlorate solution the nickel complexes are even more stable.[36]

Acknowledgments

We gratefully acknowledge Prof. Rudi van Eldik (University of Erlangen-Nürnberg, Germany) for help with the oxygen consumption measurements carried out at the University of Witten/Herdecke, Germany and the financial support from Fundação de Amparo a Pesquisa do Estado de São Paulo (FAPESP) and Conselho Nacional de Pesquisa (CNPq) (Brazilian agencies).

References

[1] C. Brandt, I. Fábián and R. van Eldik, *Inorg. Chem.*, **33**, 687, 1994.
[2] J. Berglund, S. Fronaeus and L.I. Elding, *Inorg. Chem.*, **32**, 4527, 1993.
[3] N. Coichev, K.B. Reddy and R. van Eldik, *Atmos. Environ. Part A*, **26**, 2295, 1992.
[4] N. Coichev and R. van Eldik, *New J. Chem.*, **18**, 123, 1994.
[5] C. Brandt and R. van Eldik, *Chem. Rev.*, **95**, 119, 1995 and references therein.
[6] D.W. Carlyle, *J. Am. Chem. Soc.*, **94**, 4525, 1972.
[7] J.M. Anast and D.W. Margerum, *Inorg. Chem.*, **20**, 2319, 1981.

[8] R. van Eldik and G.M. Harris, *Inorg. Chem.*, **19**, 880, 1980.
[9] M. Dellert-Ritter and R. van Eldik, *J. Chem Soc., Dalton Trans.*, 1037, 1045, 1992.
[10] S.D. Boyce, M.R. Hoffmann, P.A. Hong and L.M. Moberly, *Environ. Sci. Technol.*, **17**, 602, 1983.
[11] V.M. Bobba, G. Giraudi and E. Mentasti, *Transition Met. Chem. (London)*, **13**, 256, 1988.
[12] N. Coichev and R. van Eldik, *Inorg. Chem.*, **30**, 2375, 1991.
[13] N. Coichev and R. van Eldik, *Inorg. Chim. Acta*, **185**, 69, 1991.
[14] X. Shi, N. Dalal and K.S. Karprzak, *Environ. Health Perspect.*, **102**, 91, 1994.
[15] F. Feigel and V. Anger, *Spot Tests in Inorganic Analysis*, 6th ed., Elsevier, Amsterdam, p. 446, 1972.
[16] P. Senise, *Mikrochim. Acta*, **5**, 640, 1957.
[17] E.A. Neves, N. Coichev, J. Gebert and D. Klockow, *Fresenius Z. Anal. Chem.*, **335**, 386, 1989.
[18] S.M. Segundo, E.A. Neves and D. Klockow, *Analyst*, **119**, 1075, 1994.
[19] E.A. Neves, J. Valdes and D. Klockow, *Fresenius Z. Anal. Chem.*, **351**, 544, 1995.
[20] D.E. Linn, Jr., M.J. Dragan and D.E. Miller, *Inorg. Chem.*, **29**, 4356, 1990.
[21] D.E. Linn, Jr., S.D. Rumage and J.L. Grutsch, Jr., *Int. J. Chem. Kinet.*, **25**, 489, 1993.
[22] B. Bosnich, M.L. Tobe and G.A. Webb, *Inorg. Chem.*, **4**(8), 1109, 1965.
[23] N.F. Curtis and D.F. Cook, *Chem. Commun.*, 962, 1967.
[24] C. Brandt, N. Coichev, E. Hostert and R. van Eldik, *GIT Fachz. Lab.*, **4**, 277, 1993.
[25] R.I. Haines and A. McAuley, *Coord. Chem. Rev.*, **39**, 77, 1981.
[26] R.I. Haines and A. McAuley, *Inorg. Chem.*, **19**, 719, 1980.
[27] G. De Santis, L. Fabbrizzi, A. Poggi and A. Taglietti, *Inorg. Chem.*, **33**, 134, 1994.
[28] N. Coichev, E.A. Neves and R. van Eldik, *Inorg. Chim. Acta*, **179**, 133, 1991.
[29] J. Kraft and R. van Eldik, *Inorg. Chem.*, **28**, 2297 and 2306, 1989.
[30] D.B. Hobson, P.J. Richardson, P.J. Robinson, E.A. Hewitt and I. Smith, *J. Chem. Soc., Faraday Trans. I*, **82**, 869, 1986.
[31] A. Huss, P.K. Lim and C.A. Eckert, *J. Phys. Chem.*, **86**, 4224, 1982.
[32] OLIS KINFIT Routines, On-line Instruments Systems, Inc., Jefferson, GA, 1989.
[33] N. Coichev, R. van Eldik and D.A. Franz, *J. Chem. Educ.*, **71**(9), 767, 1994.
[34] P.W. Atkins, *Physical Chemistry*, 3rd ed., Oxford Press, Oxford, England, p. 726, 1986.
[35] F.P. Hinz and D.W. Margerum, *Inorg. Chem.*, **13**(12), 2941, 1974.
[36] A. McAuley and S. Subramanian, *Inorg. Chem.*, **30**, 371, 1991.