

Oxidation of Nickel(II) Cyclam and Tetraglycine Complexes by Dissolved Oxygen in the Presence of Sulfur(IV). Synergistic Effects of Manganese(III) and Cobalt(III)

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The autoxidation of $[\text{Ni}^{\text{II}}(\text{cyclam})]^{2+}$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) and Ni^{II} tetraglycine, accelerated by S^{IV} , is studied spectrophotometrically by following the formation of Ni^{III} complexes.

The autoxidation of Ni^{II} , accelerated by sulfur(IV) oxides, which undergoes simultaneous oxidation to S^{VI} can be followed in the presence of a suitable aqueous medium.

The chain propagation, the product formation and termination reactions are described in detail in references 12, 13 and 16.

Oxidation of $[\text{Ni}^{\text{II}}(\text{cyclam})]^{2+}$

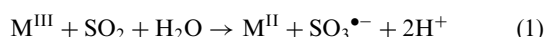
The oxidation of $[\text{Ni}^{\text{II}}(\text{cyclam})]^{2+}$ (cyclam=1,4,8,11-tetraazacyclotetradecane), accelerated by sulfur dioxide, was studied spectrophotometrically by following the formation of $[\text{Ni}^{\text{III}}(\text{cyclam})]^{3+}$ under the conditions: $[\text{Ni}^{\text{II}}(\text{cyclam})]^{2+} = 6.0 \times 10^{-3} \text{ mol L}^{-1}$; initial $[\text{Ni}^{\text{III}}(\text{cyclam})]^{3+}$, $\text{Co}^{\text{III}}_{\text{aq}}$ or $\text{Mn}^{\text{III}}_{\text{aq}} = 10^{-6} \text{ mol L}^{-1}$; $[\text{cyclam}] = 6.0 \times 10^{-3} \text{ mol L}^{-1}$; $[\text{SO}_2] = (1.0-5.0) \times 10^{-4} \text{ mol L}^{-1}$ and 1.0 mol L^{-1} perchloric acid in oxygen saturated solutions at 25°C and ionic strength = 1.0 mol^{-1} . The oxidation reaction exhibits an autocatalytic behavior in which the induction period depends on the initial $[\text{Ni}^{\text{III}}(\text{cyclam})]^{3+}$, $\text{Co}^{\text{III}}_{\text{aq}}$ and $\text{Mn}^{\text{III}}_{\text{aq}}$ concentration.

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.¹⁶ The catalytic activity is in the order $[\text{Ni}^{\text{III}}(\text{cyclam})]^{3+} > \text{Mn}^{\text{III}}_{\text{aq}} > \text{Co}^{\text{III}}_{\text{aq}}$.

The catalytic effect of the initial $[\text{Ni}^{\text{III}}(\text{cyclam})]^{3+}$, $\text{Co}^{\text{III}}_{\text{aq}}$ and $\text{Mn}^{\text{III}}_{\text{aq}}$ and the oxygen dependence show that the rate determining step is the generation of the $\text{SO}_3^{\bullet-}$ radical due to the reduction of initial metal ion in oxidation state III, M^{III} , present at very low concentration [eqn. (1)].

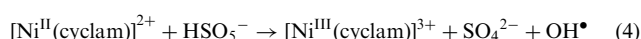
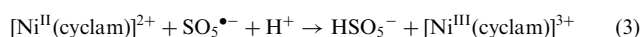
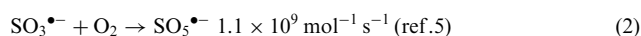
Scheme 1 Mechanism of the oxidation of $[\text{Ni}^{\text{II}}(\text{cyclam})]^{2+}$ in the presence of SO_2 and O_2 and synergistic effect of M^{III} . Main reactions:

Initiation in the presence of added $\text{M}^{\text{III}} = [\text{Ni}^{\text{III}}(\text{cyclam})]^{3+}$, $\text{Co}^{\text{III}}_{\text{aq}}$ or $\text{Mn}^{\text{III}}_{\text{aq}}$

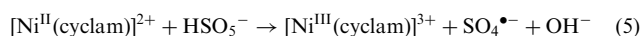


or some trace ion metal impurities such as Fe^{III} .

Autocatalysis:



or



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Autoxidation of Ni^{II} tetraglycine

The Ni^{II} tetraglycine complex, $[\text{Ni}^{\text{II}}(\text{H}_3\text{G}_4)]^{2-}$, reacts with oxygen with formation of $[\text{Ni}^{\text{III}}(\text{H}_3\text{G}_4)]^-$ and ligand oxidation.²⁵ The activation effect of sulfite was also verified at $\text{pH} = 9.2$ in air saturated solutions.

The autocatalytic nature of $[\text{Ni}^{\text{III}}(\text{H}_3\text{G}_4)]^-$ formation, in the absence of S^{IV} , can be concluded by the induction period, which increases with the tetraglycine concentration. In the presence of some initial $[\text{Ni}^{\text{III}}(\text{H}_3\text{G}_4)]^-$ and SO_3^{2-} the formation of $\text{SO}_3^{\bullet-}$ occurs [similar to eqn. (1)], which reacts with O_2 producing $\text{SO}_5^{\bullet-}$ [eqn. (2)] which oxidizes $[\text{Ni}^{\text{II}}(\text{H}_3\text{G}_4)]^{2-}$ [similar to eqn. (3)].

Although addition of trace concentrations of reducing agents, which react with $[\text{Ni}^{\text{III}}(\text{H}_3\text{G}_4)]^-$ peptide, lengthens the induction period, SO_3^{2-} accelerates the process owing to the formation of strong oxidant radicals ($\text{SO}_3^{\bullet-}$ and $\text{SO}_5^{\bullet-}$).

Technique used: UV–VIS spectroscopy

References: 39

Figures: 7

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