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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 $[Ni^{II}(cyclam)]^{2+}$ (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.

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

The oxidation of $[Ni^{II}(cyclam)]^{2+}$(cyclam=1,4,8,11-tetraazacyclotetradecane), accelerated by sulfur dioxide, was studied spectrophotometrically by following the formation of $[Ni^{III}(cyclam)]^{3+}$ under the conditions: $[Ni^{II}(cyclam)]^{2+} = 6.0 \times 10^{-3}\,mol\,L^{-1}$; initial $[Ni^{III}(cyclam)]^{3+}$, $Co^{III}{}_{aq}$ or $Mn^{III}{}_{aq} = 10^{-6}\,mol\,L^{-1}$; $[cyclam] = 6.0 \times 10^{-3}\,mol\,L^{-1}$; $[SO_2] = (1.0-5.0) \times 10^{-4}\,mol\,L^{-1}$ 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 $[Ni^{III}(cyclam)]^{3+}$, $Co^{III}{}_{aq}$ and $Mn^{III}{}_{aq}$ 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 $[Ni^{III}(cyclam)]^{3+} > Mn^{III}{}_{aq} > Co^{III}{}_{aq}$.

The catalytic effect of the initial $[Ni^{III}(cyclam)]^{3+}$, $Co^{III}{}_{aq}$ and $Mn^{III}{}_{aq}$ and the oxygen dependence show that the rate determining step is the generation of the $SO_3{}^{\bullet -}$ 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 $[Ni^{II}(cyclam)]^{2+}$ in the presence of SO_2 and O_2 and synergistic effect of M^{III}. Main reactions:

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

$$M^{III} + SO_2 + H_2O \rightarrow M^{II} + SO_3{}^{\bullet -} + 2H^+ \qquad (1)$$

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

Autocatalysis:

$$SO_3{}^{\bullet -} + O_2 \rightarrow SO_5{}^{\bullet -}\ 1.1 \times 10^9\,mol^{-1}\,s^{-1}\,(ref.5) \qquad (2)$$

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

$$[Ni^{II}(cyclam)]^{2+} + HSO_5{}^- \rightarrow [Ni^{III}(cyclam)]^{3+} + SO_4{}^{2-} + OH^{\bullet} \qquad (4)$$

or

$$[Ni^{II}(cyclam)]^{2+} + HSO_5{}^- \rightarrow [Ni^{III}(cyclam)]^{3+} + SO_4{}^{\bullet -} + OH^- \qquad (5)$$

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

Autoxidation of Ni^{II}tetraglycine

The Ni^{II} tetraglycine complex, $[Ni^{II}(H_{-3}G_4)]^{2-}$, reacts with oxygen with formation of $[Ni^{III}(H_{-3}G_4)]^-$ and ligand oxidation.[25] The activation effect of sulfite was also verified at pH = 9.2 in air saturated solutions.

The autocatalytic nature of $[Ni^{III}(H_{-3}G_4)]^-$ 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 $[Ni^{III}(H_{-3}G_4)]^-$ and $SO_3{}^{2-}$ the formation of $SO_3{}^{\bullet -}$ occurs [similar to eqn. (1)], which reacts with O_2 producing $SO_5{}^{\bullet -}$ [eqn. (2)] which oxidizes $[Ni^{II}(H_{-3}G_4)]^{2-}$ [similar to eqn. (3)].

Although addition of trace concentrations of reducing agents, which react with $[Ni^{III}(H_{-3}G_4)]^-$ peptide, lengthens the induction period, $SO_3{}^{2-}$ accelerates the process owing to the formation of strong oxidant radicals ($SO_3{}^{\bullet -}$ and $SO_5{}^{\bullet -}$).

Technique used: UV–VIS spectroscopy

References: 39

Figures: 7

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