The Effect of NO on the Kinetics and Mechanism of Oxidation of Amines and Peptides by Central Ni(III) Ions

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Recently it was suggested that Ni(III)(cyclam), Ni³⁺L, oxidizes NH₂CH₃ via:

Ni³⁺L(H₂O)²⁺ + 2NH₂CH₃ ↔ LNi³⁺(NH₂CH₃)₂⁺ + H⁺ ↔ LNi³⁺(NHCH₃)(NH₂CH₃)²⁺

In parallel it was shown that intramolecular reductive nitrosylation of a Cu²⁺(cyclam-derivative) results in the N-nitrolysation of the cyclam ligand. It seemed therefore of interest to study the effect of NO on the rate of oxidation of NH₂CH₃ by Ni³⁺L. Indeed the addition of NO to the reaction mixture accelerates considerably the reaction rate and changes the rate law from second order to first order in Ni³⁺L. Furthermore the observed rate constant is proportional to [OH⁻] in the pH range 4-7. Similar effects are obtained when NO is added to a solution containing Ni³⁺(glycylglycylglycine). The results suggest that also in these systems reductive N-nitrolysation takes place. Analogous experiments with Cu(III)(peptide) are in progress.