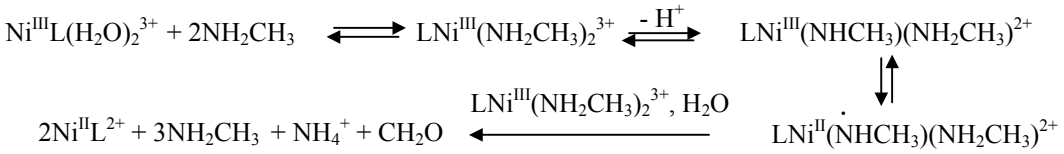
The Effect of NO on the Kinetics and Mechanism of Oxidation of Amines and Peptides by Central Ni(III) Ions

Dror Shamir[1], Israel Zilbermann[1,2], Eric Maimon[1,2], Haim Cohen [1,3] and Dan Meyerstein[1,3]

1. Chemistry Department, Ben-Gurion University of the Negev, Beer-Sheva, Israel;
2. Nuclear Research Centre Negev, Beer-Sheva, Israel;
3. Biological Chemistry Department, College of Judea and Samaria, Ariel, Israel

Recently it was suggested that Ni(III)(cyclam), $Ni^{III}L$, oxidizes NH_2CH_3 via:



In parallel it was shown that intramolecular reductive nitrosylation of a Cu"(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 NH_2CH_3 by $Ni^{III}L$. 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 $Ni^{III}L$. 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 Ni^{III}(glycylglycylglycine). The results suggest that also in these systems reductive N-nitrolysation takes place. Analogous experiments with Cu(III)(peptide) are in progress.