

The Kinetics of Hydrogen-Induced Ligand-Substitution for Tris(ethylenediamine) Nickel (II) in Water

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Abstract:

When Tris(ethylenediamine) Nickel (II) is dissolved in an aqueous solution, the introduction of a strong acid will break the coordinate bonds between the ethylenediamine ligands and their central nickel atom and allow water molecules to coordinate with the nickel instead. Using a Stopped-Flow to observe the rates and absorbance spectra of the ligand substitution allowed for the kinetics and rate laws of the reaction. The analysis of the reaction showed that the overall reaction consisted of three irreversible stepwise reactions, with each stepwise reaction involving a single ethylenediamine molecule being replaced by two water molecules. The component spectra and concentration profiles of the four coordination complexes were observed over time and rate laws were determined. Using each reaction's rate law, a set of equations were developed that model the concentration of each complex over time and the rate constants were determined. With the d8 octahedral electron splitting of nickel(II) and the unique component spectra of each coordination complex, the energy difference between each higher and lower energy d-orbital set was calculated.

Introduction:

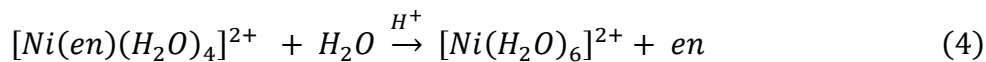
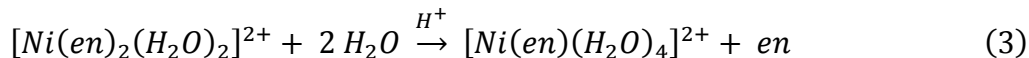
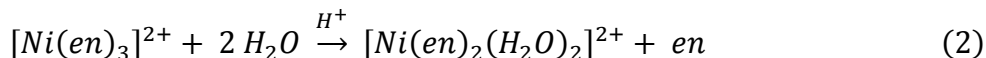
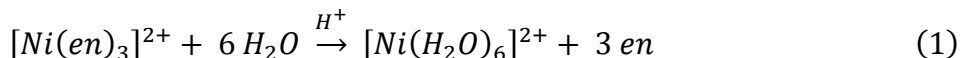
Ethylenediamine is a very strong, bidentate ligand; up to three ethylenediamine molecules can form coordinate bonds with a single nickel(II) ion. As stronger field ligands will readily replace weaker field ligands in a coordination complex, when ethylenediamine is added to an aqueous solution of hexaaqua nickel (II), each ethylenediamine molecule will replace two of the water molecules coordinated to the nickel ion, forming tris(ethylenediamine) nickel (II). For a weaker ligand to replace a stronger ligand in a coordination complex, the coordinate bond between the stronger ligand and the metal ion must be broken in such a way that the coordinate bond won't reform. Because the nitrogen atoms in ethylenediamine are Brønsted-Lowry bases, when tris(ethylenediamine) nickel(II) is dissolved in an acidic aqueous solution, the hydrogen ions will bond to the nitrogen atoms in each ethylenediamine molecule, breaking the coordinate covalent bonds between each ethylenediamine and the nickel(II) ion and allowing water molecules to coordinate with the nickel(II) ion instead, forming hexaaqua nickel(II) (eq. 1).¹

This hydrogen-induced transition from tris(ethylenediamine) nickel(II) to hexaaqua nickel(II) involves three consecutive reactions. First, tris(ethylenediamine) nickel(II) loses a single ethylenediamine molecule and gains two water molecules, becoming di(aqua)-bis(ethylenediamine) nickel(II) (eq. 2). Next, the di(aqua)bis(ethylenediamine) nickel(II) loses another ethylenediamine molecule and gains two additional water molecules, becoming tetra(aqua)ethylenediamine nickel(II) (eq. 3). Finally, the tetra(aqua)ethylenediamine nickel(II) loses its final ethylenediamine molecule and gains another two water molecules and becomes hexaaqua nickel(II) (eq. 4).

Ligand strength is based on how strongly the ligand's electrons interact with the electrons of the d-orbitals in the central metal ion, with stronger ligands creating a greater energy difference in the metal's d-orbitals. Nickel has a d8 octahedral electron splitting configuration, with three

lower t_{2g} orbitals, and two higher e_g orbitals. Because nickel (II) has 8 d-orbital electrons, the lower t_{2g} orbitals will be full when the nickel is bonded to strong field ligands and when it's bonded to weak field ligands, and leaving two electrons in the e_g orbitals. With each of the e_g orbitals only half-filled, a photon of the correct energy can excite an electron in one of the t_{2g} orbitals into the e_g orbitals; it takes an even higher energy photon to excite a second electron from the t_{2g} orbitals to fill the final space in the e_g orbitals. The energy difference, Δ_o , can be found using spectrophotometry as the wavelengths of greatest absorbance occur when the photons of that wavelength have identical energies as the Δ_o (eq. 5). With photons of two different energy values required to excite electrons into filling the e_g orbitals, nickel experiences two different absorbance values in its component spectra.

Ethylenediamine is a much stronger field ligand than water, so as each ethylenediamine is replaced by two water molecules there is a decrease in the Δ_o between the e_g and the t_{2g} orbitals, and thus an increase in the wavelength of maximum absorbance for the complex's component spectra. Given that there's a linear correlation between absorbance and concentration, measuring the absorbance values allows for the concentration of each complex to be found as well. A stopped-flow can measure in the ultraviolet and visible spectrum one thousand times per second, so by running the reaction through a stopped-flow, the concentration of each complex can be found each millisecond. By observing the concentration of each complex over time, a rate law can be found for each reaction.



$$\Delta_o = hc/\lambda \quad (5)$$

Experimental

Reagents of the highest quality were used. Tris(ethylenediamine) nickel(II) chloride was synthesized by dissolving reagent grade hexaaqua nickel(II) chloride in deionized water and adding an excess of ethylenediamine. The tris(ethylenediamine) nickel(II) chloride was separated through vacuum filtration and purified through recrystallization. The stock of dry crystalline tris(ethylenediamine) nickel(II) chloride was stored in a desiccator prior to use. The stock of 2.00M hydrochloric acid was created by diluting concentrated hydrochloric acid with deionized water.

Solutions of tris(ethylenediamine) nickel(II) chloride were mixed with solutions of hydrochloric acid inside an SX20 Stopped-Flow from Applied Photophysics. Table 1 describes the different molarities of the two solutions as they were mixed together. The stopped-flow utilized a photodiode array (PDA) to obtain the component spectra between 180 and 725nm for the reactions, recorded the absorbance values every 0.02000 seconds, and computed concentration

profiles for the four nickel complexes over a twenty second interval. Varying the concentrations of the tris(ethylenediamine) nickel(II) chloride and hydrochloric acid solutions allowed the Method of Initial Rates to be used to determine the order of the reactants. Similarly, plotting out the negative logarithm of the concentration profiles vs time allowed integrated rate laws for each reaction to also be found. Multiple runs of the same molarity concentrations were done in order to more accurately determine the modified rate constants for each reaction.

Table 1. Reactant Molarity Combinations

[HCl]	$[Ni(en)_3]Cl_2$
1.00 M	0.1000 M
1.00 M	0.2000 M
1.00 M	0.0500 M
2.00 M	0.1000 M
0.50 M	0.1000 M

Calculations and Results:

The basic structure of the rate laws describing the reactions of equations 2, 3, and 4 are detailed by equations 6, 7, and 8 respectively. Because the concentration of water is not noticeably changed during the reaction, the rate constants k_1 , k_2 , and k_3 and the unchanging concentration of water can be used to create modified rate constants, k'_1 , k'_2 , and k'_3 respectively (eq. 9). The method of initial rates can be used to determine the order of each nickel complex, a_n (eq. 10), and the order of the hydrogen ions in each rate law, b_n (eq. 11). The integrated rate laws were used to confirm the overall order of each reaction's rate laws (Figure 1 and eq. 12, 13, & 14) and the value of each modified rate constant; with the reactions run through the stopped-flow over one hundred times, each modified rate constant, k'_n , was calculated at 99% confidence along with each half-life, λ , and each coefficient of variation, CV (Table 2). The modified rate laws for the reactions are described in equations 15, 16, and 17.

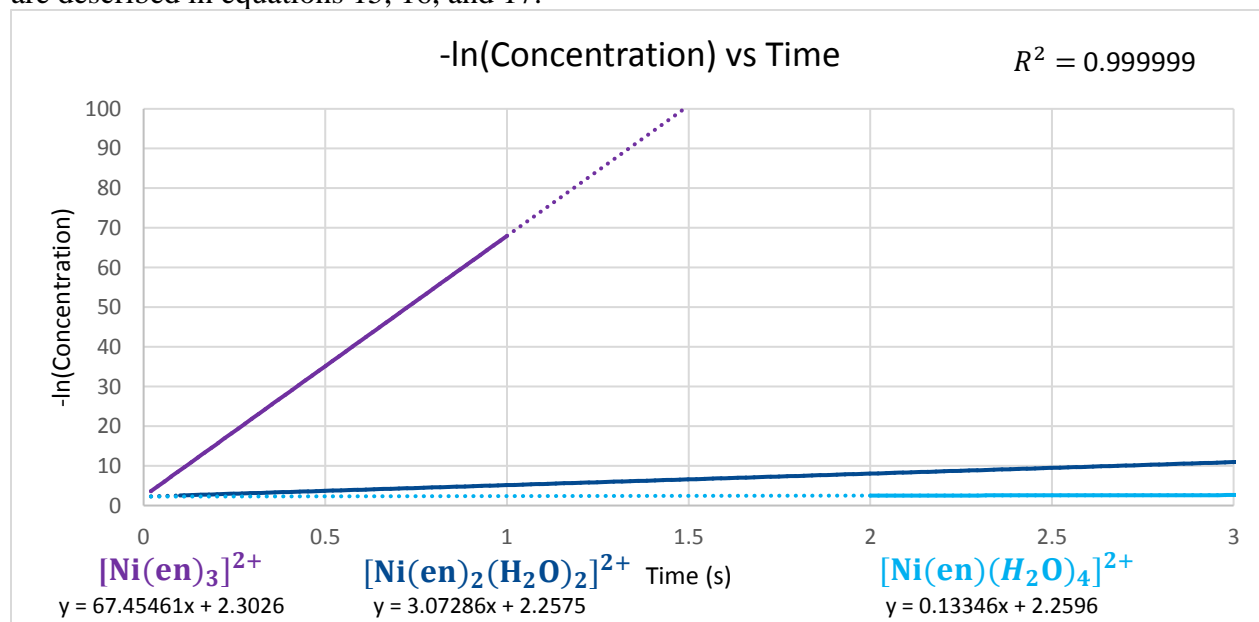


Figure 1. Integrated Rate Law Plot for the Initial Reactant and both Intermediates

Table 2. Modified Rate Constants, Half-Lives, and Coefficients of Variation

	k'_n (seconds ⁻¹)	λ (seconds)	CV
k'_1	67.45461 ± 0.66978	0.0103	0.0378
k'_2	3.07286 ± 0.02616	0.2256	0.0324
k'_3	0.13346 ± 0.00121	5.1938	0.0344

$$Rate_1 = k_1 * [Ni(en)_3^{2+}]^{a_1} [H^+]^{b_1} [H_2O]^{c_1} \quad (6)$$

$$Rate_2 = k_2 * [Ni(en)_2(H_2O)_2^{2+}]^{a_2} [H^+]^{b_2} [H_2O]^{c_2} \quad (7)$$

$$Rate_3 = k_3 * [Ni(en)(H_2O)_4^{2+}]^{a_3} [H^+]^{b_3} [H_2O]^{c_3} \quad (8)$$

$$k'_n = k_n * [H_2O]^{c_n} \quad (9)$$

$$a_n = a_1 = a_2 = a_3 = 1 \quad (10)$$

$$b_n = b_1 = b_2 = b_3 = 0 \quad (11)$$

$$\ln[Ni(en)_3]_t = -k'_1 t + \ln[Ni(en)_3]_0 \quad (12)$$

$$\ln[Ni(en)_2(H_2O)_2]_t = -k'_2 t + \ln[Ni(en)_2(H_2O)_2]_0 \quad (13)$$

$$\ln[Ni(en)(H_2O)_4]_t = -k'_3 t + \ln[Ni(en)(H_2O)_4]_0 \quad (14)$$

$$Rate_1 = k'_1 * [Ni(en)_3^{2+}] \quad (15)$$

$$Rate_2 = k'_2 * [Ni(en)_2(H_2O)_2^{2+}] \quad (16)$$

$$Rate_3 = k'_3 * [Ni(en)(H_2O)_4^{2+}] \quad (17)$$

Each nickel (II) complex has two values of maximum absorption at wavelengths that correspond to the Δ_o energy values of splitting between the e_g and t_{2g} orbitals. Because water is a weaker ligand than ethylenediamine, the Δ_o energy gap between the e_g and t_{2g} orbitals decreases as each ethylenediamine molecule is replaced by two water molecules, increasing the wavelengths of maximum absorption. The Δ_o values were calculated using equation 5. The wavelengths of maximum absorption are listed on Figure 2 and their corresponding Δ_o values are listed on Table 3.

Table 3. Absorption Wavelengths and Δ_o Values

Complex	λ_1 (nm)	Δ_o (J)	λ_1 (nm)	Δ_o (J)
$[Ni(en)_3]^{2+}$	339.483	$5.85 * 10^{-19}$	534.262	$3.72 * 10^{-19}$
$[Ni(en)_2(H_2O)_2]^{2+}$	356.615	$5.57 * 10^{-19}$	569.717	$3.49 * 10^{-19}$
$[Ni(en)(H_2O)_4]^{2+}$	371.575	$5.35 * 10^{-19}$	623.619	$3.19 * 10^{-19}$
$[Ni(H_2O)_6]^{2+}$	395.026	$5.03 * 10^{-19}$	715.986	$2.77 * 10^{-19}$

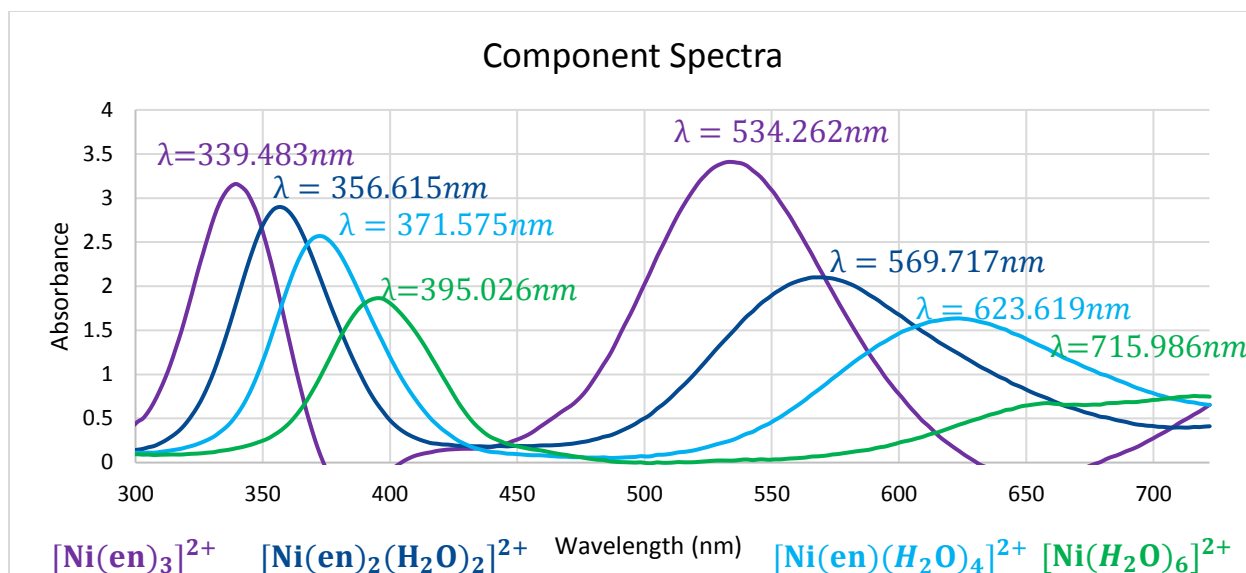


Figure 2. Component Spectra and Wavelengths of Maximum Absorbance

Given that each rate law is first order, the three consecutive, irreversible reactions can be described as a series of four differential equations (eq. 18, 19, 20, & 21). The solutions to these differential equations (eq. 22, 23, 24, & 25 respectively) mathematically model the concentration of the complexes as a function of time, assuming that the concentrations of the intermediates and the final product were initially zero. While equations modeling two consecutive, irreversible reactions have been previously published, equations modeling three consecutive, irreversible reactions have not.² Plugging the values for the modified rate constants and initial concentrations of the nickel complexes into the modeling equations lead to predicted values accurate to within five significant figures. Figure 3 shows the concentration profile of initial reactant, both intermediates, and the final product as found by the Stopped-Flow. In the concentration profile, the initial reactant, $[Ni(en)_3]^{2+}$ is completely used up in the first few hundredths of a second while the first intermediate, $[Ni(en)_2(H_2O)_2]^{2+}$ is produced and used up in less than two seconds.

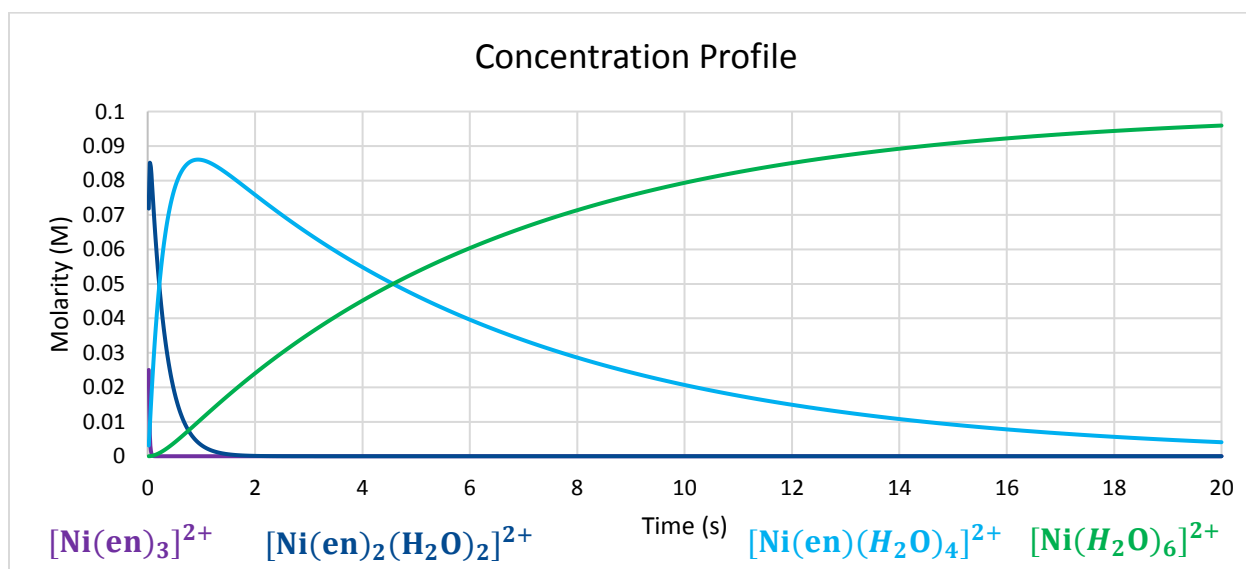


Figure 3. Concentration Profile of Initial Reactant, Both Intermediates, and the Final Product

$$\frac{d[Ni(en)_3]_t}{dt} = -k'_1[Ni(en)_3]_t \quad (18)$$

$$\frac{d[Ni(en)_2(H_2O)_2]_t}{dt} = k'_1[Ni(en)_3]_t - k'_2[Ni(en)_2(H_2O)_2]_t \quad (19)$$

$$\frac{d[Ni(en)(H_2O)_4]_t}{dt} = k'_2[Ni(en)_2(H_2O)_2]_t - k'_3[Ni(en)(H_2O)_4]_t \quad (20)$$

$$\frac{d[Ni(H_2O)_6]_t}{dt} = k'_3[Ni(en)(H_2O)_4]_t \quad (21)$$

$$[Ni(en)_3]_t = [Ni(en)_3]_0 e^{-k'_1 t} \quad (22)$$

$$[Ni(en)_2(H_2O)_2]_t = [Ni(en)_3]_0 \left(\frac{k'_1}{k'_2 - k'_1} \right) (e^{-k'_1 t} - e^{-k'_2 t}) \quad (23)$$

$$[Ni(en)(H_2O)_4]_t = [Ni(en)_3]_0 \left(\frac{k'_1 k'_2}{k'_2 - k'_1} \right) \left(\frac{e^{-k'_1 t}}{(k'_3 - k'_1)} - \frac{e^{-k'_2 t}}{(k'_3 - k'_2)} + \frac{(k'_2 - k'_1)e^{-k'_3 t}}{(k'_3 - k'_2)(k'_3 - k'_1)} \right) \quad (24)$$

$$[Ni(H_2O)_6]_t = [Ni(en)_3]_0 \left(1 - \frac{k'_3 k'_2 e^{-k'_1 t}}{(k'_2 - k'_1)(k'_3 - k'_1)} + \frac{k'_3 k'_1 e^{-k'_2 t}}{(k'_2 - k'_1)(k'_3 - k'_2)} - \frac{k'_2 k'_1 e^{-k'_3 t}}{(k'_3 - k'_2)(k'_3 - k'_1)} \right) \quad (25)$$

A generic system of 3 consecutive, irreversible reactions (eq. 26) can be described by a series of differential equations (eq. 27, 28, 29, & 30). The solutions to these differential equations (eq. 31, 32, 33, & 34) describes the concentrations of A, B, C, and D as a function of time for any initial set of concentrations.



$$\frac{dA_t}{dt} = -k_1 A_t \quad (27)$$

$$\frac{dB}{dt} = k_1 A_t - k_2 B_t \quad (28)$$

$$\frac{dC_t}{dt} = k_2 B_t - k_3 C_t \quad (29)$$

$$\frac{dD_t}{dt} = k_3 C_t \quad (30)$$

$$A_t = A_0 e^{-k_1 t} \quad (31)$$

$$B_t = \frac{A k_1}{(k_2 - k_1)} (e^{-k_1 t} - e^{-k_2 t}) + B_0 e^{-k_2 t} \quad (32)$$

$$C_t = \frac{A_0 k_2 k_1}{(k_2 - k_1)} \left(\frac{e^{-k_1 t} - e^{-k_3 t}}{(k_3 - k_1)} - \frac{e^{-k_2 t} - e^{-k_3 t}}{(k_3 - k_2)} \right) + \frac{B_0 k_2}{(k_3 - k_2)} (e^{-k_2 t} - e^{-k_3 t}) + C_0 e^{-k_3 t} \quad (33)$$

$$D_t = A_0 \left(\frac{k_2}{k_2 - k_1} \left(1 + \frac{k_3 e^{-k_1 t} - k_1 e^{-k_3 t}}{(k_3 - k_1)} \right) - \frac{k_1}{k_2 - k_1} \left(1 + \frac{k_2 e^{-k_3 t} - k_3 e^{-k_2 t}}{(k_3 - k_2)} \right) \right) + B_0 \left(1 + \frac{k_2 e^{-k_3 t} - k_3 e^{-k_2 t}}{(k_3 - k_2)} \right) + C_0 (1 - e^{-k_3 t}) + D_0 \quad (34)$$

References:

1. Melvin, William et al. "The Kinetics of Substitution Reactions of Poly(ethylenamine)nickel(II) Complexes" *Inorganic Chemistry*, Volume 11, No 3., 1972, p488-493
2. Jackson, W.G. et al. "Consecutive, Irreversible First-Order Reactions. Ambiguities and Practical Aspects of Kinetic Analyses." *International Journal of Chemical Kinetics*, Volume 9, 1977, p535-548