

Title: **Kinetics and mechanism of the reactions of chromium(III) with biological amino acids: L-histidine**

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Date: January 2019

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The kinetics of the reaction of substitution of aqua ligands in chromium(III) complexes by the basic amino acid L-histidine, in aqueous media and under slightly acidic conditions (pH 3.60 – 5.79), has been studied with the aid of a spectrophotometric technique (at 530 nm). The rate-time profiles showed an initial acceleration period followed by a deceleration one. A three consecutive reaction model has been applied involving two long-lived intermediates (not reactive enough to be in steady state), rate constants k_1 , k_2 and k_3 corresponding to the successive decays of the reactant, the first long-lived intermediate and the second, respectively. The three rate constants increased when the medium ionic strength was raised using KNO_3 as background electrolyte, whereas the effect of KCl was of minor intensity, and decreased as the HCl initial concentration increased (base catalysis). The average values of the activation energies at different pHs were 60 ± 17 (for k_1), 94 ± 6 (for k_2) and 93 ± 5 (for k_3) kJ mol^{-1} . The UV-Vis spectrum of the first long-lived intermediate was rather close to that of the inorganic reactant, whereas the spectrum of the second long-lived intermediate was somehow in between those corresponding to the inorganic reactant and the reaction product. The spectra of the final reacting mixtures revealed the co-existence of at least two complexes differing in the number of organic ligands, along with the corresponding protonated forms. A mechanism in agreement with the available experimental data has been proposed, involving the previous activation of the Cr(III) starting complex by deprotonation, as well as three rate-determining (slow) steps in which the breakage of a Cr(III) -aqua chemical bond takes place, thus leaving a vacant place for the coordination of the organic ligand.

Keywords: chromium(III), complexation reaction, kinetics, L-histidine, long-lived intermediates